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Formation of a Detached Plume from a Cement Plant

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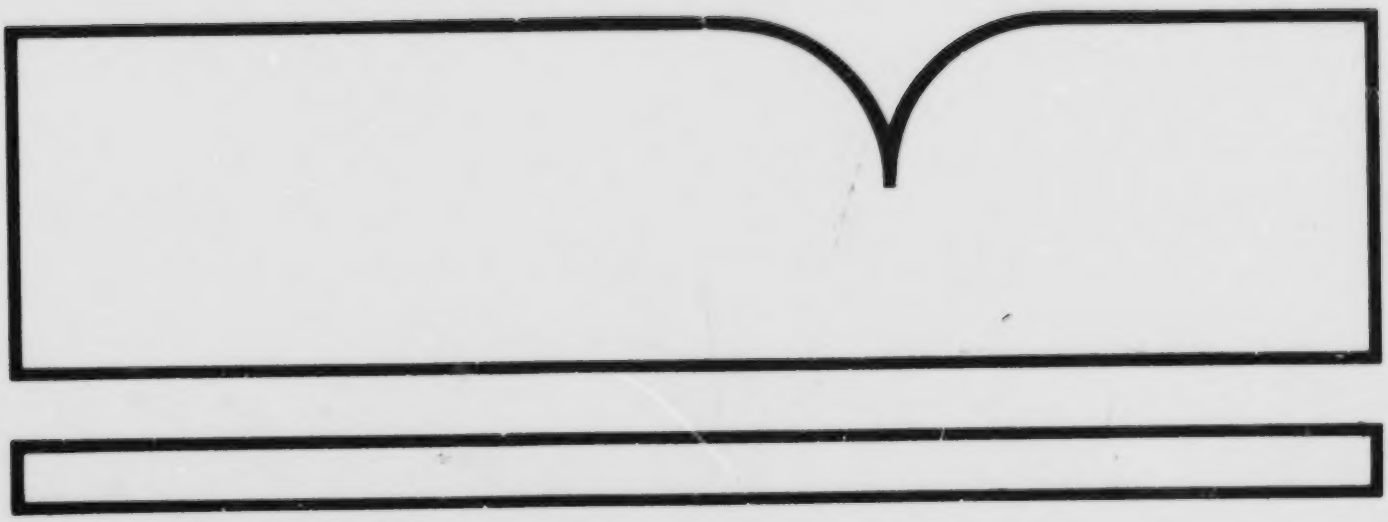

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FORMATION OF A DETACHED PLUME FROM A CEMENT PLANT

by

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Comparison of the results from the plume and source measurement indicated the formation of the plume was the result of the reaction of ammonia and hydrochloric acid. The formation of ammonium chloride occurred within the same set of reaction parameters as independent laborabory studies had previously indicated.

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CONTENTS

Abstract iii
Figures vi
Tables vii
Acknowledgment ix

1. Introduction 1
   Background 1
   Scope of the Problem 3
2. Conclusions 6
3. Experimental 8
   Description of sampling strategy 8
   Measurement methods 11
      Optical 11
      Tethered balloon 12
      Source sampling for particles 12
      Source sampling for gases 13
      Process sampling 14
4. Results 15
   Plume measurements 15
   Opacity 15
      Plume sampling with tethered balloons 18
      Scanning electron microscopy analysis 24
   Source Measurements 31
      Sampling schedule 31
      Gases 36
      Particles 47
      Process sampling 67
5. Discussion 73

References 77

FIGURES

Number		Page
1	Flow scheme for cement production plant	4
2	Port arrangement for extractive gas and particle sampling	9
3	Sampling arrangement for gaseous emissions measurements with the ROSE system	10
4	Results of LIDAR, measurements on a detached plume	16
5	Relative locations of Lidar, source, and wind directions	17
6	Results of SEM analysis of May 5 filter, background	26
7	Results of SEM analysis of May 5 filter	28
8	Results of SEM analysis of May 5 filter, in plume	29
9	Results of SEM analysis of May 5 filter, in plume	30
10	Results of SEM analysis of May 7 filter, in plume	32
11	Results of SEM analysis of May 7 filter, in plume	33
12	Results of SEM analysis of May 7 filter, background	34
13	Particle size distribution for Pilat run No. 2 (no filter)	49
14	Particle size distribution for Pilat run No. 2 (with filter)	50
15	Particle size distribution for Pilat runs No. 5, 6, 7 (with filters)	51
16	Particle size distribution for Pilat runs No. 2 and 5, 6, 7 average (no filter)	52
17	Particle size distribution for Pilat runs No. 2 and 5, 6, and 7 average (with filter)	53
18	Comparison of Pilat results for bypass and mill modes	55

TABLES

Number		Page
1	Schedule of Balloon Sampling of the Plume	19
2	Results of XRF Analysis of 1 μm Fluoropore Plume Filter Samples	21
3	Results of IC Analysis of Three-Stage Filters from Plume Sampling	22
4	Distribution of Cl^-, NH_3, and SO_x in TFT	23
5	Results of Sulfite Sampling of a Plume	25
6	Schedule of Source Sampling	35
7	Velocity Traverses for Cement Plant Stack	37
8	Results of NH_3 Sampling	38
9	Results of HCl Sampling	40
10	Results of Total Sulfate Analysis of SO_x Samples	41
11	Results of Other Gaseous Measurements	44
12	Results of ROSE Optical Measurements	45
13	Mass Emission Rates for Conventionally Measured Compounds	46
14	Results of Particulate Sampling at a Cement Plant	48
15	Results of XRF Analysis of Pilat Sample No. 1	56
16	Results of XRF Analysis of Pilat Sample No. 2	57
17	Results of XRF Analysis of Pilat Sample No. 3	58
18	Results of XRF Analysis of Pilat Sample No. 5	59
19	Results of XRF Analysis of Pilat Sample No. 6	60
20	Results of XRF Analysis of Pilat Sample No. 7	61
21	Results of XRF Analysis of Source Particulate Characterization Sample No. 1	62

Number		Page
22	Results of XRF Analysis of Source Particulate Characterization Sample No. 2	63
23	Results of XRF Analysis of Source Particulate Characterization Sample No. 3	64
24	Results of XRF Analysis of Source Particulate Characterization Sample No. 4	65
25	Results of XRF Analysis of Source Particulate Characterization Sample No. 5	66
26	Process Data	68
27	Results of Chemical Analyses of Process Samples	69
28	Ammonia Contents of Raw Products	70

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A study at this level, involving several separate working groups performing as a team, deserves special recognition. Considering the lack of cooperation from the weather, the crowded working conditions on the stack, the haste necessary to confirm some of the plume sampling methodologies prior to sampling, and the uncertainty of the plant operation mode, only a well coordinated group of professionals could have succeeded this well. The authors, therefore, wish to acknowledge the following for their efforts in the study:

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SECTION 1

INTRODUCTION

BACKGROUND

Visible emissions of particulate matter from stationary sources are addressed in the EPA Code of Federal Regulations (CFR-40, Chapter 1, p. 360. Chapter 1). For opaque plumes, visible emissions can be determined by trained observers, according to Reference Method 9 (1); or by optical measurements using a Light Detection and Ranging (LIDAR) Method (2). For certain new sources, regulations require the opacity of an emission gas stream to be measured by continuous, in-stack opacity monitors as described in the Federal Register, Vol. 39, No. 177, Part II, Wednesday, September 11, 1974, P. 32852. Most new sources are subject to particulate matter regulations measured by both opacity and particulate mass loading.

For some sources, however, problems exist even when these requirements are met. These problems involve a plume which becomes visibly opaque some distance from the point of emission. The term "detached plume" has been coined for this phenomenon. The detached plume presents special problems to Regional Enforcement personnel, inasmuch as NSPS requirements are being met, but the public still sees the visible plume. It has become apparent that, in addition to water condensation, the phenomenon can involve the reaction of gaseous components of the emissions after leaving the stack.

Such a detached plume was the subject of a Technical Assistance request from Enforcement personnel of EPA Region II in May 1979. The plume involved

a Portland cement production plant, burning a residual fuel oil to fire the kiln. In response to the request, the Stationary Sources Emissions Research Branch (SSERB) of the Environmental Sciences Research Laboratory (ESRL), in cooperation with the Industrial Environmental Research Laboratory (IERL), conducted an extensive source-plume measurement program. The objective of the study was to determine the nature of the reaction of these source emissions which resulted in the detached visible plume. The results of that study are available from several literature publications (3,4,5,). Those results suggested the formation of ammonium sulfur salts in the water droplets of the plume.

In November of 1980 a similar Technical Assistance request was issued from Region IV Enforcement to the ESRL (6). This request also addressed the need to study the cause of a detached plume at a Portland cement plant. The kiln at this source, however, was fired with coal, rather than fuel oil, and the likely explanation which applied to the oil-fired kiln in Region II seemed inapplicable for this source.

The SSERB again responded to the request by establishing a research program to study the cement plant emissions. After agreement on a sampling protocol with the Region IV personnel, and scheduling a test period satisfactory with plant operation and management, a study was conducted in May of 1981. This study, as with the Region II cement plant, addressed the source emissions and the possible reactions of some of the components of that emission to form a visible plume some distance from the plant. Simultaneous source-plume sampling was conducted in order to understand the plume formation phenomenon. This report describes the operations, the research measurement approach, the results of the measurements, and finally, some interpretation of these results.

SCOPE OF THE PROBLEM

The Lehigh Portland Cement Company, located in the Town of Leeds, Alabama, is situated between two hilly ridges in the Cahaba Valley, approximately 10 miles east of Birmingham. The plant is a coal-fired, rotary kiln type process, adjacent to the quarry from which the main component of the raw materials is derived. A material and combustion gas flow scheme is shown in Figure 1. The raw product components are mixed and then ground by the mill. During milling, the products are subjected to the kiln exit gases after they pass through the heat exchanger (riser). The ground raw material is carried by the gas flow to the electrostatic precipitator (ESP), where it is recovered and conveyed to the storage bins. Storage bin material (milled feed supply) is continually fed through the riser (preheater) system to the kiln for clinker formation. During passage through the riser, the product is preheated prior to its entrance into the kiln while the kiln exhaust gas is cooled from approximately 1900°F to 600°F. The 600°F gas then enters the mill during normal operations. Passage of the riser exit gas through the mill results in an additional gas temperature drop of nearly 400°F, such that the ESP receives the gas around 200°F. During normal production when the mill is in operation, compliance with in-stack opacity and mass loadings is met. Since the kiln start-up and shut-down involve long periods of time, as well as severely disrupting production, it is desirable to run the kiln as continuously as possible. The purpose of the ground raw product storage silos is to assure an available supply of kiln feed material in the event of a mill shut-down. When down-time occurs for the mill, the riser exit gas must be redirected to the ESP by an alternate route. In the absence of the raw feed product in the mill to absorb the heat energy, the gas stream must be cooled by some other means prior to its entrance into the ESP. This is achieved by directing the riser gas stream through the cooling tower, which lowers the temperature to an acceptable level for the ESP. As the kiln

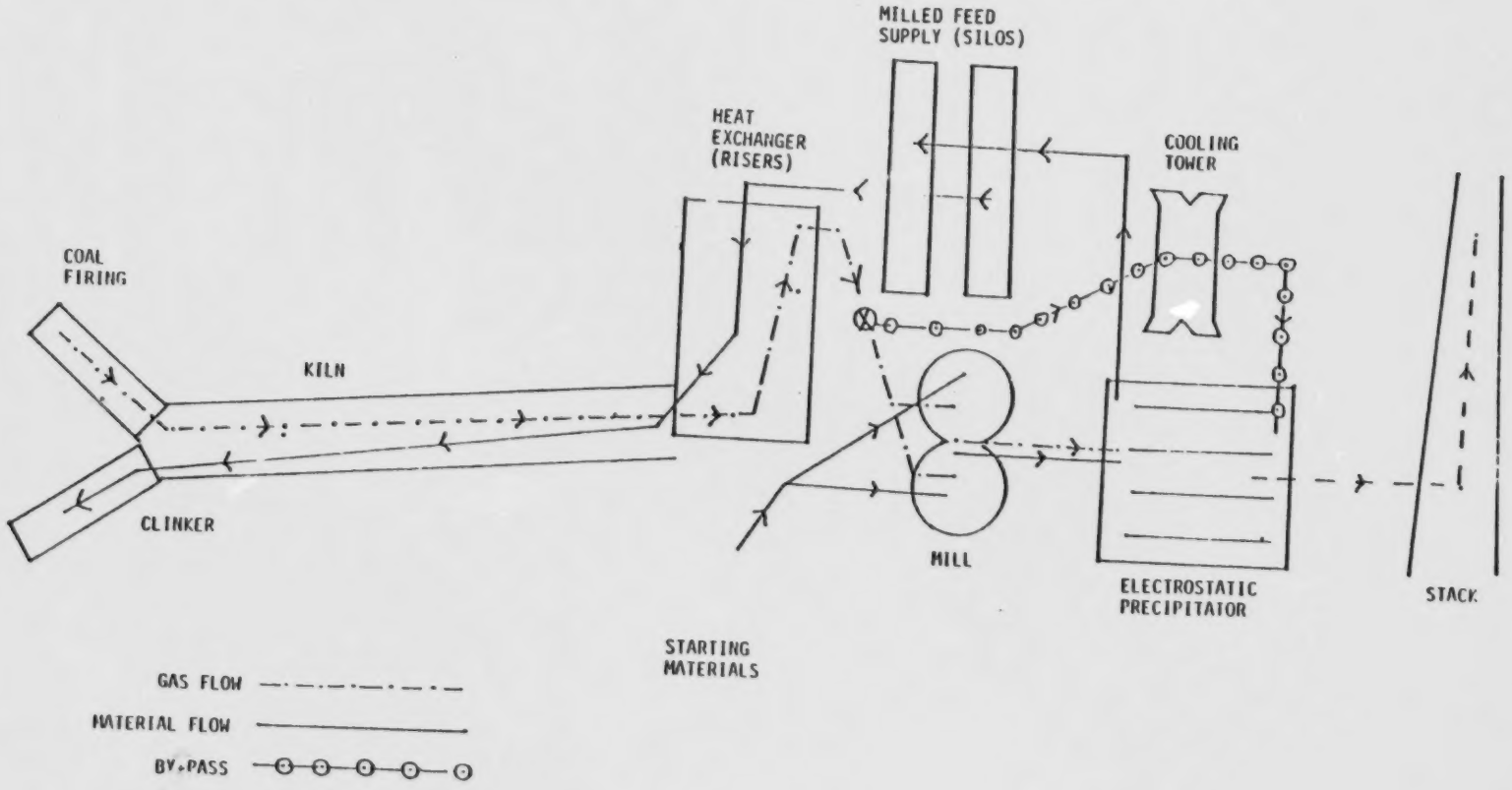


Figure 1. Flow scheme for cement production plant.

exit gas carries some of the raw material through the riser heat exchanger, a heavily particle-laden air stream enters the cooling tower, resulting in absorption of some of the particles by the cooling water. The wet particles drop out the bottom of the tower in the form of sludge. From the cooling tower the exhaust gas enters the ESP, where most of the remaining particles are recovered from the gas stream and transported to the storage silo. The detached plume phenomenon occurs during this bypass mode, when the in-stack opacity is well below 10% and the particulate mass loading is well within compliance. Following the exit of the exhaust gas from the 100 ft tall, 8 ft diameter stack, some type of conversion occurs and an opaque plume develops. The cause of this detached plume development in the bypass mode is the object of this study.

SECTION 2

CONCLUSIONS

Comparison of the data from both source and plume measurements involving both gas and particles indicates that the detached plume formation results from the reaction of gaseous ammonia (NH_3) and hydrochloric acid (HCl) in the plume. An average of 16.3 ppm of gaseous NH_3 and 12.4 ppm of gaseous HCl were emitted during the bypass mode. This can be contrasted to the emission of 2.4 ppm gaseous NH_3 and 12.9 ppm gaseous HCl during the mill mode when no detached plume exists.

Virtually all of the sulfur oxides are emitted as sulfur dioxide (SO_2) from the source. While the molar ratio of SO_2 to NH_3 was found to be 10, there was little association between the two gases in the plume samples.

The results from a three-stage filter system sampling in the plume during the bypass mode indicated nearly 60% of the chloride ion (Cl^-) was retained in particles on the first filter, with both Cl^- and NH_3 exceeding the sulfur presence by at least a 17:1 ratio.

Analysis by electron microscopy of these filters indicated the presence of ammonium chloride (NH_4Cl) salt in the bypass mode plume samples. The analysis indicated that the particle size of the NH_4Cl crystals was predominantly between 0.2 and 0.6 μm.

A comparison was made between the Triple Filter Train results and the increasing opacity of the plume as its distance from the source increased. This opacity increase, as measured with the LIDAR, indicated an ongoing reaction whereby the particle density of the plume was increasing up to 44 m from the emission point.

Analysis of the milled product, which acts to collect some of the gaseous emissions from the kiln, showed a temperature relationship between NH_3 absorption and desorption, with greater desorption at higher temperatures. From these results, and the fact that the ESP operates at higher temperatures during the bypass mode than during the mill mode, higher NH_3 emission is expected during the bypass mode. A comparison of the physical and chemical properties of a similar gaseous NH_3-HCl system studied which was recently published shows that such a reaction is likely and is the cause of the plume opacity.

SECTION 3

EXPERIMENTAL

DESCRIPTION OF SAMPLING STRATEGY

Source sampling was conducted on the permanently installed platform through six accessible 4-in sampling ports. Two sampling inlets were occupied throughout the test period by a Lear-Siegler Model RM41 opacity monitor. A permanent recording of the stack opacity is available at the control room within the plant. A schematic of the sampling port arrangement, with the sampling that was conducted at each respective port, is shown in Figure 2. In addition, optical transmission tests with a Remote Optical Sensing of Emissions (ROSE) system (to be discussed later) required two ports for a cross-stack light path. The arrangement of the light source for those measurements is shown in Figure 3.

The sampling during the study involved several facets of research, all focusing on the principal problem of the detached plume formation. In general, the sampling can be categorized as gaseous or particulate, bypass or mill mode, and at source or plume site. Attempts were made to perform all particle sampling and gaseous measurements simultaneously.

The initial sampling protocol included sampling three 4-hr periods in the mill mode of operation, and sampling four 3-hr periods in the bypass mode. Meeting these sampling objectives was chiefly controlled by two factors: the weather (source and plume sampling could not be performed in rain), and by plant operation, which on many occasions automatically goes to the bypass mode

A Conventional methods for NH_3, HCl

B EPA Method 5
EPA Method 6

C ROSE method with port F

D Particle characterization

E EPA Method 7 (NO_x)
SO_x by MACS
Other research methods

F Particle sizing (Pilat)

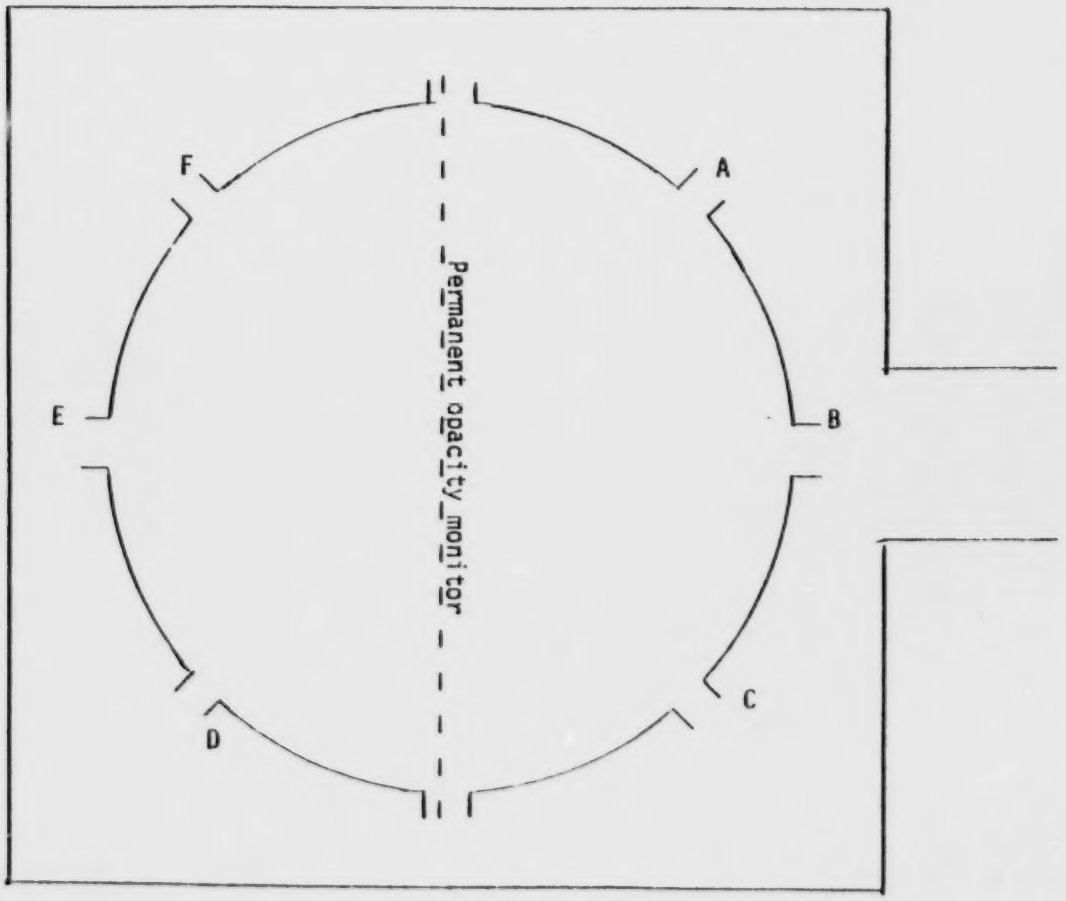


Figure 2. Port arrangement for extractive gas and particle sampling.

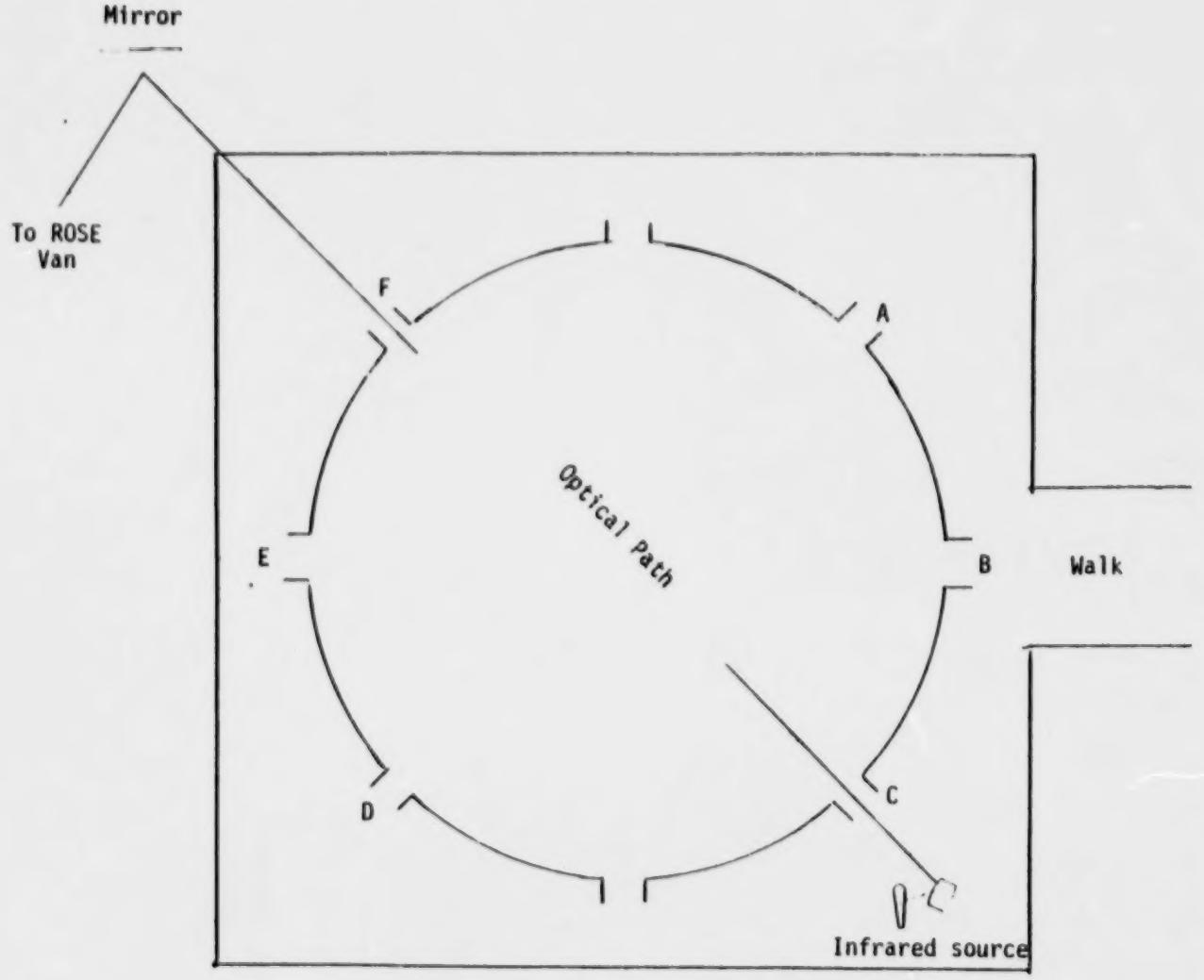


Figure 3. Sampling arrangement for gaseous emissions measurements with ROSE system.

due to unscheduled and unavoidable malfunction in the mill mode equipment. Because of problems with both of these factors, the entire sampling plan was not totally completed. The first day of set-up and testing on Monday afternoon was somewhat limited by electrical failures and extra time needed to compensate for the crowded stack conditions. A limited series of samples was collected in the mill mode on Monday. On Tuesday the plant went into the bypass mode as planned from approximately 8 a.m. to 4:30 p.m., after which the plant returned to the mill mode and cross-stack optical measurements using the ROSE system were performed. At approximately 9 p.m. Tuesday, after the ROSE measurements had been completed, a malfunction in the mill mode forced the plant to operate in the bypass mode all night until 6 a.m. Wednesday. When sampling was to start on Wednesday, rain threatened and two electric fields of the ESP were malfunctioning. Sampling was held up until 11 a.m., at which time it became apparent that the kiln feed would have to be stopped, the ESP cooled, and proper maintenance performed. Since this would require a minimum of 3 hr, sampling for Wednesday was called off. Because the material supply in the silos was severely depleted during the bypass mode usage on Tuesday, the scheduled bypass mode operation on Thursday was cancelled. Instead, the mill mode sampling which had been scheduled for Wednesday was conducted on Thursday. A brief bypass mode sampling period was achieved on Friday by part of the sampling team.

MEASUREMENT METHODS

Optical

Two remote optical measurements were performed during the study: plume opacity with the LIDAR system (2) and in-stack source gas concentrations with the Remote Optical Sensing of Emissions (ROSE) system (7). The ROSE system measures the concentrations of various gaseous components in a source by

Fourier Transform Infrared (FTIR) spectroscopy. By passing an infrared beam through the gas in the stack or through the plume, a wide range of infrared-active gases can be detected.

Tethered Balloon

Sampling in the plume, involved filters suspended from tethered, helium-filled balloons. Measurements and equipment used for plume sampling have been described in other work (8). In this study, since the stack was only 100 ft high, sample gas was pulled through the filters by a vacuum transfer line connected to a pump on the ground. Particles and gases were collected on the appropriate media suspended from the balloons, and the sample gas volumes were recorded from the metered pump box on the ground. Telemetry accompanying the balloon provided temperature and humidity data on a ground level printout.

Three types of filtering approaches were used during plume sampling. A triple filter train (TFT), consisting of a 1.0 μm Fluoropore prefilter to collect particles: a potassium hydroxide (KOH) impregnated cellulose filter to collect gaseous HCl, and a cellulose filter impregnated with oxalic acid to collect gaseous NH_3, was used. The laboratory studies attesting to validity of this method has been described previously (9). A second sampling approach involved a formalin treated cellulose filter for stabilizing sulfite ion (SSS) (10).

The third approach to plume sampling with the tethered balloons involved particle collection on 0.4-μm and 0.8-μm Nuclepore filters. The filters were subjected to the well established procedure of scanning electron microscopy for particle sizing and composition determinations (11).

Source Sampling for Particles

Source sampling was conducted both by established methodology and experimental approaches. The mass particulate loading was determined by Reference Method 5 (12). Particulate sizing and characterization were performed by using

a Pilat impactor (13) and a series of filtering media, coupled with both x-ray fluorescence (XRF) (14) and other chemical analyses of the collected particles. The elemental content of both the filter and sized particle samples were measured by XRF. For the Pilat impactor, particles from the separate fractions were transferred after weighing from the impactor plates to polycarbonate film via pentane sonication and evaporation (Pilat redeposition procedure).

Six separate types of characterization filters were used for a cross-sectional measurement of particle composition. These were glass fiber filters, Millipore AA (0.8 μm), Nuclepore (0.8 μm), Millipore FSLW (3 μm), SSS TE37 (1 μm), and Ghia Dual Teflon (1 μm). The advantages and disadvantages of these filters for x-ray analysis and source characterization work are well documented (15). In summary, however, six separate types of filters were used for source-particulate characterization measurements in order to compromise between the advantages and disadvantages offered by the six collectively.

Source Sampling for Gases

Gaseous source sampling was performed for oxides of nitrogen (NO_x), oxides of sulfur (SO_x), sulfuric acid (H_2SO_4), HCl, hydrofluoric acid (HF), and NH_3. In addition, Orsat analysis was conducted to measure carbon dioxide (CO_2) and oxygen (O_2). According to EPA Method 3 (16), NO_x was determined by EPA Reference Method 7 (17), and SO_x was determined by the EPA Reference Method 6 (18) with some modification. This modification is needed since for sources with NH_3 a partial absorption of the SO_2 occurs in the first impinger containing the 80% isopropanol/20% H_2O (IPA) solution (4). To determine total SO_2, the amount measured in the peroxide impingers is added to the sulfur measured in the IPA impinger. In order to determine total sulfur, the sulfate catch of the probe plug was also measured. H_2SO_4 was measured with a miniature acid condensation (19) system (MACS). In this sampling system sulfuric acid is collected in a temperature controlled glass plug subsequent to a high temperature quartz

filter. HCl and HF are determined by absorption into 0.1 N NaOH solutions in a midget impinger system. The probe plug used in this extractive sampling was also analyzed for Cl^-. NH_3 determinations were performed by absorbing NH_3 in midget impingers containing 0.1 N H_2SO_4. The probe plug preceding the 0.1 N H_2SO_4 impinger solution was analyzed for NH_3. Both HCl and NH_3 were also measured by a modified version of the MACS train. With this measurement approach, the stack gas filtration is accomplished with a flat quartz filter rather than the conventional glass wool probe plug. Since the flat filter should minimize any gas-solid reactions which may occur on the conventional probe plug, some simultaneous sampling with the two different methods was necessary. The general source sampling program was directed toward the cross-checking of simultaneously conducted measurement methods for a better estimation of the cause of the visible plume.

Process Sampling

Samples from strategic locations within the process confines were acquired to provide information concerning material mass balances. Operating data, including fuel and feed stock usage rates, were obtained. Coal samples, along with feed samples from the milled feed supply, were taken on a composite basis. Input water and output sludge samples from the conditioning tower were also composited. To assure no loss of NH_3, a 0.1 N aliquot of H_2SO_4 solution was added to the sludge samples.

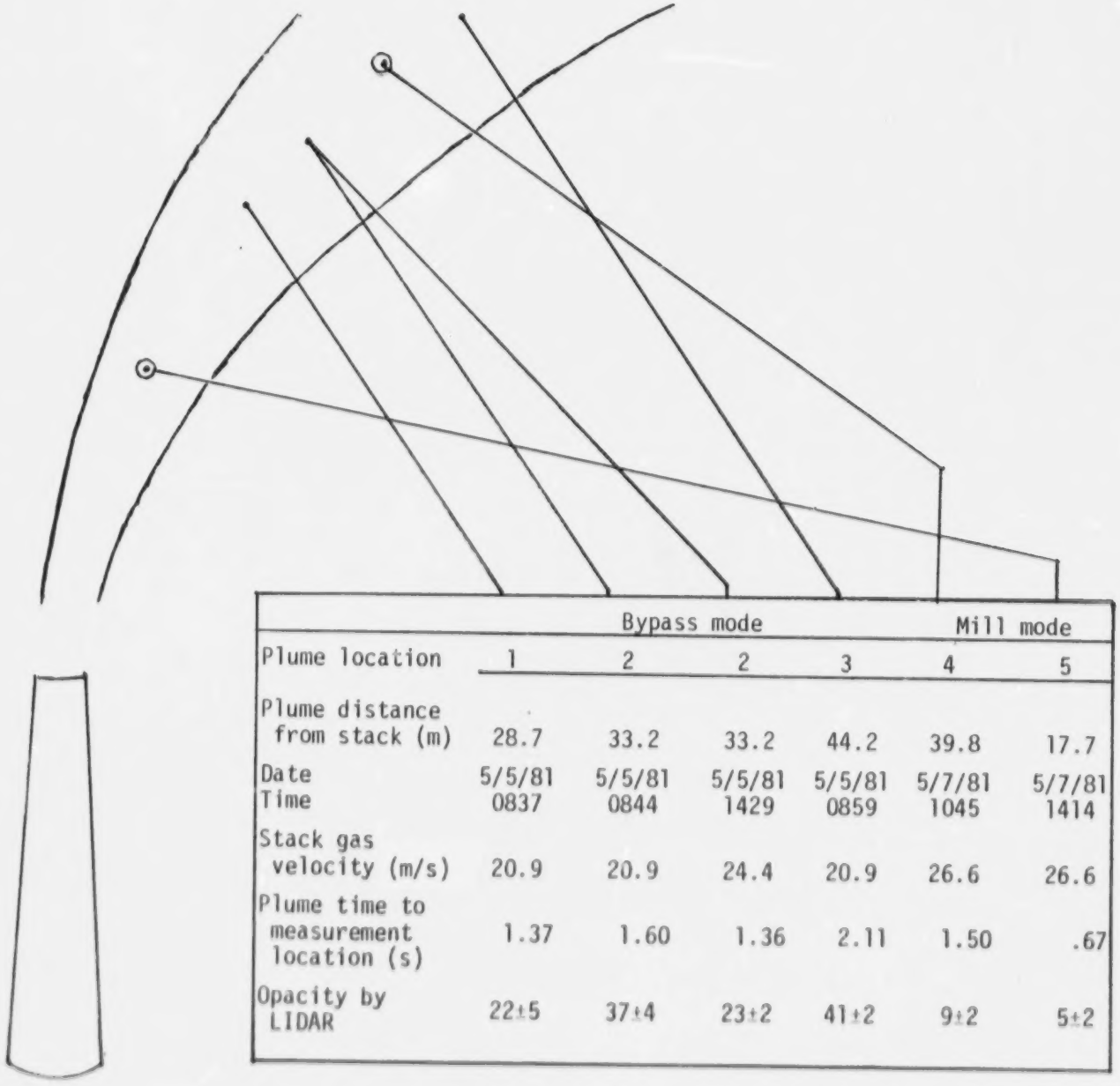
SECTION 4

RESULTS

PLUME MEASUREMENTS

Opacity

Opacity measurements were performed during both mill and bypass modes. Opacity measurements with the LIDAR system during the bypass mode were conducted at various times on Tuesday and during the mill mode on Thursday. The results of these opacity measurements, along with a depiction of how the measurements were performed, are shown in Figures 4 and 5. As the data in Figure 4 indicate, opacities were measured at five distinct distances from the stack exit, and arbitrarily assigned a location number for reference purposes. After the plant switched to the bypass mode on Tuesday, three series of opacities were measured from 8:37 to 8:59 a.m. During this same time, visual observations confirmed increasing opacity of the plume as the distance from the stack increased. The LIDAR opacities in Figure 4 are the result of 13, 16, and 14 separate measurements at 8:37, 8:44 and 8:59 a.m., respectively. As it was possible to determine visually that the nature of the plume formation had changed later in the bypass mode operation, a second measurement at location 2 was made at 2:29 p.m. A total of 22 separate measurements gave an opacity of 23 ± 2 for the afternoon measurement. Two separate opacity determinations of the plume were performed during the mill mode on Thursday. The results shown in Figure 4 for 10:45 a.m. and 2:14 p.m. involved a total of 16 and 18 separate determinations, respectively. The plume on Thursday was barely visible to the naked eye. The LIDAR data confirm the very low opacities for both the morning and afternoon measurements.



	Bypass mode				Mill mode	
Plume location	1	2	2	3	4	5
Plume distance from stack (m)	28.7	33.2	33.2	44.2	39.8	17.7
Date	5/5/81	5/5/81	5/5/81	5/5/81	5/7/81	5/7/81
Time	0837	0844	1429	0859	1045	1414
Stack gas velocity (m/s)	20.9	20.9	24.4	20.9	26.6	26.6
Plume time to measurement location (s)	1.37	1.60	1.36	2.11	1.50	.67
Opacity by LIDAR	22±5	37±4	23±2	41±2	9±2	5±2

Figure 4. Results of LIDAR measurements on a detached plume

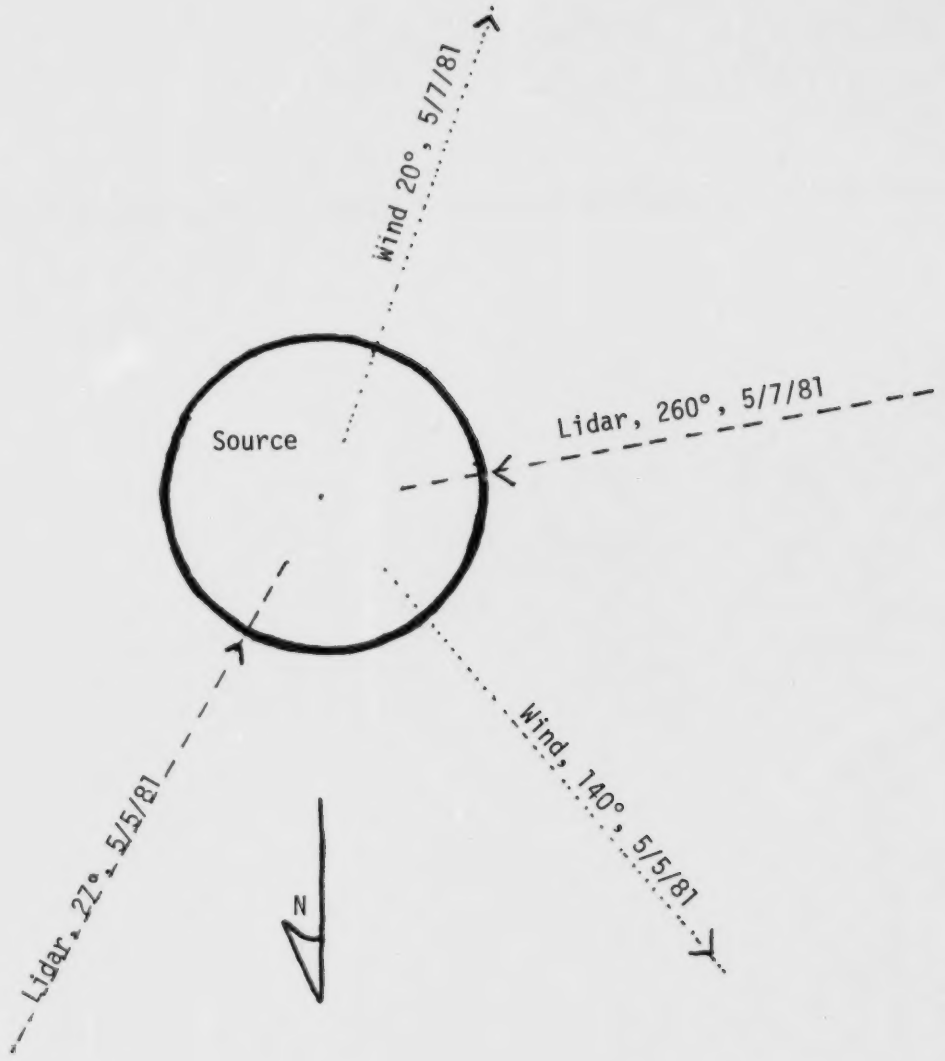


Figure 5. Relative locations of LIDAR, source, and wind directions

The Figure 4 data include stack gas velocities determined by Pitot tube and transverse measurements, and estimates of the time involved for the plume to travel from the stack exit to the point of opacity determination. These data were calculated from the corresponding stack gas velocities and measurement point distances from the stack, assuming no velocity change for the stack gas. While this assumption is not exactly correct, it does provide a relative time frame. One interesting observation from the data is the decrease in opacity at location 2 between 8:44 a.m. and 2:29 p.m. on Tuesday. While this difference could be attributed to a number of causes that might influence gaseous reaction rates in a plume, it may simply be due to plume velocity, since the estimated travel time to this measurement location more nearly matches the location 1 measurement with a similar estimated travel time. Hence, plume velocity may be the cause of various opacity readings at this point for the two different times of measurements.

Plume Sampling with Tethered Balloons

A total of 30 individual filter samples were collected either within or as background to the plume as shown in Table 1. During the test period six TFT readings were obtained. Both samples collected on Tuesday during the bypass mode were within the plume. Four filters were collected on Thursday during the mill mode; two in and two out of the plume. Prior to analyses by ion chromatography (IC), the 1.0-μm Fluoropore prefilters were submitted for elemental analysis by XRF. The results of the analyses, in terms of the most abundant elements detected, are shown in Table 2. Cl^- was the predominant element collected in particulate matter for both samples on Tuesday. As NH_3 can react with either HCl or SO_2, it is of interest that for these two plume samples in the bypass mode the ratio of Cl^- to S was 29.3 and 28.6 for the first filter. Assuming that whatever is on the prefilter was collected as particles, chloride

TABLE 1. SCHEDULE OF BALLOON SAMPLING OF THE PLUME

Glass Filter

Date	Time	(Plume)	Δ t (min)	Δ V_3 (ft^3)	Temp (°F)	RH (%)
5/4/81			60	34.950		
5/5/81			61	22.104		
5/7/81	13:00	In	63	48.777	61	81
5/7/81	13:00	Out	63	50.590	61	81

Nuclepore

Date	Time	(Plume)	Size (μm)	Δ T (min)	Δ V_3 (ft^3)	Temp (°F)	RH (%)
5/4/81	16:46-16:56	In	0.8	10	4.650	81	41
5/4/81	17:06-17:16	In	0.4	10	5.771	81	41
5/4/81		Out	0.8	10	5.311		
5/4/81		Out	0.4	10	4.869		
5/5/81	11:25-11:30	In	0.8	5	1.581	79	37
5/5/81	14:51-15:01	Out	0.4	10	2.024	79	47
5/5/81	15:06-15:11	In	0.8	5	1.596	79	47
5/5/81	15:28-15:38	In	0.4	10	2.047	79	34
5/6/81	10:17-10:22	In	0.4	5	1.060	68	80
5/6/81	10:36-10:42	In	0.8	6	1.942	68	80
5/7/81	12:28-12:38	In	0.8	10	7.046	68	69
5/7/81	12:28-12:38	Out	0.8	10	7.327	68	64
5/7/81	16:49-16:59	In	0.8	10	7.922	70	69
5/7/81	16:49-16:59	Out	0.8	10	8.397	70	64

Three Stage - XRF Prefilter

Date	Time	(Plume)	Δ t (min)	Δ V_3 (ft^3)	Temp (°F)	RH (%)
5/5/81	10:00-11:01	In	61	17.977	75	46
5/5/81	11:37-12:44	In	67	14.183	81	37
5/7/81	9:46-10:46	In	60	7.614	69	76
5/7/81	9:46-10:46	Out	60	15.227	67	65
5/7/81	14:19-15:24	In	65	34.227	69	76
5/7/81	14:19-15:24	Out	65	32.981	69	65

Sulfite Stabilization Filter

5/5/81	8:17- 9:36	In	79	21.222	69	57
5/5/81	14:18-15:00	In	42	14.970	79	47
5/7/81	11:06-12:06	In	60	43.420	67	70
5/7/81	11:06-12:06	Out	60	46.094	67	70
5/7/81	15:38-16:38	In	60	44.674	68	64
5/7/81	15:38-16:38	Out	60	46.734	68	64

TABLE 2. RESULTS OF XRF ANALYSIS OF PLUME FILTER[a] SAMPLES

Sample ID	Date	Volume[b]	Plume	Elements detected, decreasing abundance → µg[c]							
Bypass Mode											
TFT-11	5/5/81	18.0	In	Cl 45.3	Ca 10.2	Mg 2.91	Sr 2.35	Si 2.03	S 1.54	Fe 1.15	Al 0.82
TFT-12	5/5/81	14.2	In	Cl 37.0	Ca 9.6	Si 2.00	S 0.96	Al 0.76	Fe 0.74	K 0.54	Mg 0.17
Mill Mode											
TFT-13	5/7/81	7.6	In	Ca 13.1	Si 1.63	S 1.56	Fe 0.96	Al 0.76	Cl 0.71	K 0.37	Mg 0.17
TFT-2	5/7/81	33.0	Out	S 3.51	Ca 1.89	Si 0.74	Fe 0.34	Al 0.17	Sn 0.15	K 0.12	Mg 0.07
TFT-14	5/7/81	34.2	In	Ca 30.5	Si 4.70	S 4.34	Fe 2.76	Al 2.20	K 1.02		
TFT-1	5/7/81	15.2	Out	S 0.18	Ca 0.07						

[a] 1.0 µ Fluoropore

[b] actual cubic feet

[c] assuming 8.55 cm^2 collection area of 37 mm filter

salt appears far more abundant than sulfite or sulfate salts. For TFT samples collected on Thursday, little Cl^- was found on the prefilter in contrast to sulfur, the third most abundant element found.

Following XRF, the TFT filters were submitted to IC analyses for Cl^-, NH_3, NO_3^-, $SO_3^=$, and $SO_4^=$. The results of these ion analyses for the series of six samples are presented in Table 3. Good agreement between the two analysis methods is obtained for Cl^- on the first filter. It was not evident why the TFT-2 background sample showed 1.05 µg of Cl^- by the IC method but not by XRF. For samples TFT-14 ard TFT-1, the 0.56 and 0.06 µg of Cl^- measured by IC was below the minimum detectable limit of the XRF. Since the XRF does not identify elements by chemical species, comparison between XRF and IC analyses of the sulfur catch on the prefilters must be done by converting the masses of $SO_3^=$ and $SO_4^=$ to moles of sulfur. Table 4 shows the masses of S detected by IC and the conversion of $SO_3^=$ and $SO_4^=$ mass from the first filter to moles of sulfur. The sulfur catch on the prefilters of TFT-11 and TFT-12 are low for the XRF method relative to the IC method. For the other four first filter catches, the elemental sulfur results compare well for the two methods. Table 4 also shows the percent of NH_3 and Cl^- present on the prefilter relative to the total filter catches. Assuming all prefilter catch as particulate matter, roughly 62% of the Cl^- is present as particulate matter during the bypass mode. More variation is noted for the percent ammonia on the prefilter for the bypass mode day. The TFT-11 and TFT-12 samples were collected between 10:00 and 11:01 a.m. and between 11:37 a.m. and 12:44 p.m., respectively. It is difficult to interpret the large variation between the 65.8 and 25.3% collection of NH_3 on the prefilters for these two samples. Table 4 also shows the molar amounts of Cl^-, NH_3 and S for the prefilters. It must be pointed out that none of the sulfur retained by the KOH filter is assumed to be particulate sulfur. The sulfur, reported as $SO_3^=$ and $SO_4^=$ in Table 3 is the result of SO_2 passing through the

TABLE 3. RESULTS OF IC ANALYSIS OF THREE-STAGE FILTERS FROM PLUME SAMPLING

Sample	Date	Volume[a]	Veff[b]	Total µg from filter							
				First filter				Second filter			Th rd filter
				Cl^-	NH_3	$SO_3^=$	$SO_4^=$	Cl^-	$SO_3^=$	$SO_4^=$	NH_3
Bypass Mode											
TFT-11	5/5	18.0	12.1	45.79	12.67	2.44	5.34	22.21	327	801	6.57
TFT-12	5/5	14.2	7.1	34.11	11.78	.74	4.46	25.91	870	446	34.71
Mill Mode											
TFT-13	5/7	7.6	5.17	.80	2.92	.98	4.58	1.19	ND	166	3.25
TFT-2	5/7	33.0	--	1.05	12.52	ND	11.51	.26	ND	ND	ND
TFT-14	5/7	34.2	7.18	.56	9.29	2.29	14.88	1.44	163	314	22.41
TFT-1	5/7	15.2	--	.06	4.87	ND	.51	.05	ND	ND	3.67

[a]Actual air volume in ft^3

[b]Sample corrected to estimate actual plume volume collected by Vol eff = Actual Volume x $\frac{\text{time in plume}}{\text{total sampling time}}$

TABLE 4. DISTRIBUTION OF Cl^-, NH_3 AND SO_x IN TFT

Sample	Date	Plume	Total µg[a]					% on first filter		First filter (µ moles)		
			Cl^-	NH_3	$SO_3^=$	$SO_4^=$	S[b]	Cl^-	NH_3	Cl^-	NH_3	S[c]
Bypass Mode												
TFT-11	5/5	In	68.0	19.24	2.44	5.34	2.76	67.3	65.8	1.90	1.16	.08
TFT-12	5/5	In	60.0	46.49	.74	4.46	1.79	56.9	25.3	1.71	2.73	.06
Mill Mode												
TFT-13	5/7	In	1.99	6.17	.98	4.58	1.92	40.2	47.3	.06	.44	.06
TFT-2	5/7	Out	1.31	12.52	ND	11.51	3.84	80.1	100.0	3.70	.89	.12
TFT-14	5/7	In	2.50	31.70	2.29	14.88	5.88	2.24	29.3	7.10	2.26	.18
TFT-1	5/7	Out	.11	8.5	ND	.51	.17	54.5	57.2	--	.61	.01

[a] Adding all 3 filters for NH_3 and Cl^-, but counting only sulfur species on the first filter

[b] Sulfur from both $SO_3^=$ and $SO_4^=$ on the first filter

[c] Sulfur from both $SO_3^=$ and $SO_4^=$ on the first filter

prefilter. An interesting comparison is the moles of sulfur on the prefilter to that of Cl^- or NH_3 from Table 4 for the bypass mode. Calculations of the amounts of S from SO_2 retained by the KOH filter for TFT-11 and TFT-12 give 12.4 and 15.5 μ moles, respectively. This means that sulfur is present in a molar ratio of 10:1 for NH_3 for TFT-11 compared to 1.6:1 for Cl^-.

The results of the formalin-treated SSS filters for $SO_3^=$ collection and retention are presented in Table 5. Very little $SO_3^=$ was collected during the earliest sample on Tuesday. An excessive amount of $SO_4^=$ for the same sample was collected relative to the similar TFT-11 sample. For the SSS samples, only the $SO_4^=$ from the earliest background samples of Thursday agreed well with the similar TFT samples. The high results of nearly all the SSS filters relative to TFT filters could not be explained, and further investigation appears warranted for the application of the method.

Scanning Electron Microscopy Analysis

A total of 14 filters involving both in-plume and background samples were collected on Nuclepore filters for SEM analyses. As the preferred pore size or the exact amount of loading, were unknown, both 0.4- and 0.8-μm filters were used. In order to acquire a proper filter loading, both large and small volume samples were acquired from the plume. As a result, only some of the 14 filters were selected for analyses, based on the number of particles present on the filters. Emphasis was placed on filters collected on Tuesday during the bypass mode and on Thursday, when the most representative mill mode sampling of the source was conducted.

For the four samples collected during the bypass mode, three were from within the plume and one was background. As indicated in Figure 6, the particle sizes ranged from 0.5 to 6.0 μm for the background sample. Over half the particles were pollen (not shown), and the remaining particles were carbonaceous materials. One plume sample (11:25 to 11:30 a.m.) was collected

TABLE 5. RESULTS OF SULFITE SAMPLING OF A PLUME

Date	Time	Plume	Vol[a]	Veff[b]	Sulfite µg	Sulfate µg
	Bypass Mode					
5/5	08:17 - 09:36	In	21.2	Unknown	0.89	15.16
5/5	14:18 - 15:00	In	15.0	10.1	18.40	21.12
	Mill Mode					
5/7	11:06 - 12:06	In	43.4	17.8	10.38	22.56
5/7	11:06 - 12:06	Out	46.1	--	--	13.37
5/7	15:38 - 16:38	In	44.7	29.9	5.35	32.91
5/7	15:38 - 16:38	Out	46.7	--	--	19.40

[a]Actual air volume in ft^3

[b]Sample volume corrected to estimate actual plume volume collected by

$$\text{Veff} = \text{Actual Volume} \times \frac{\text{time in plume}}{\text{total sampling time}}$$

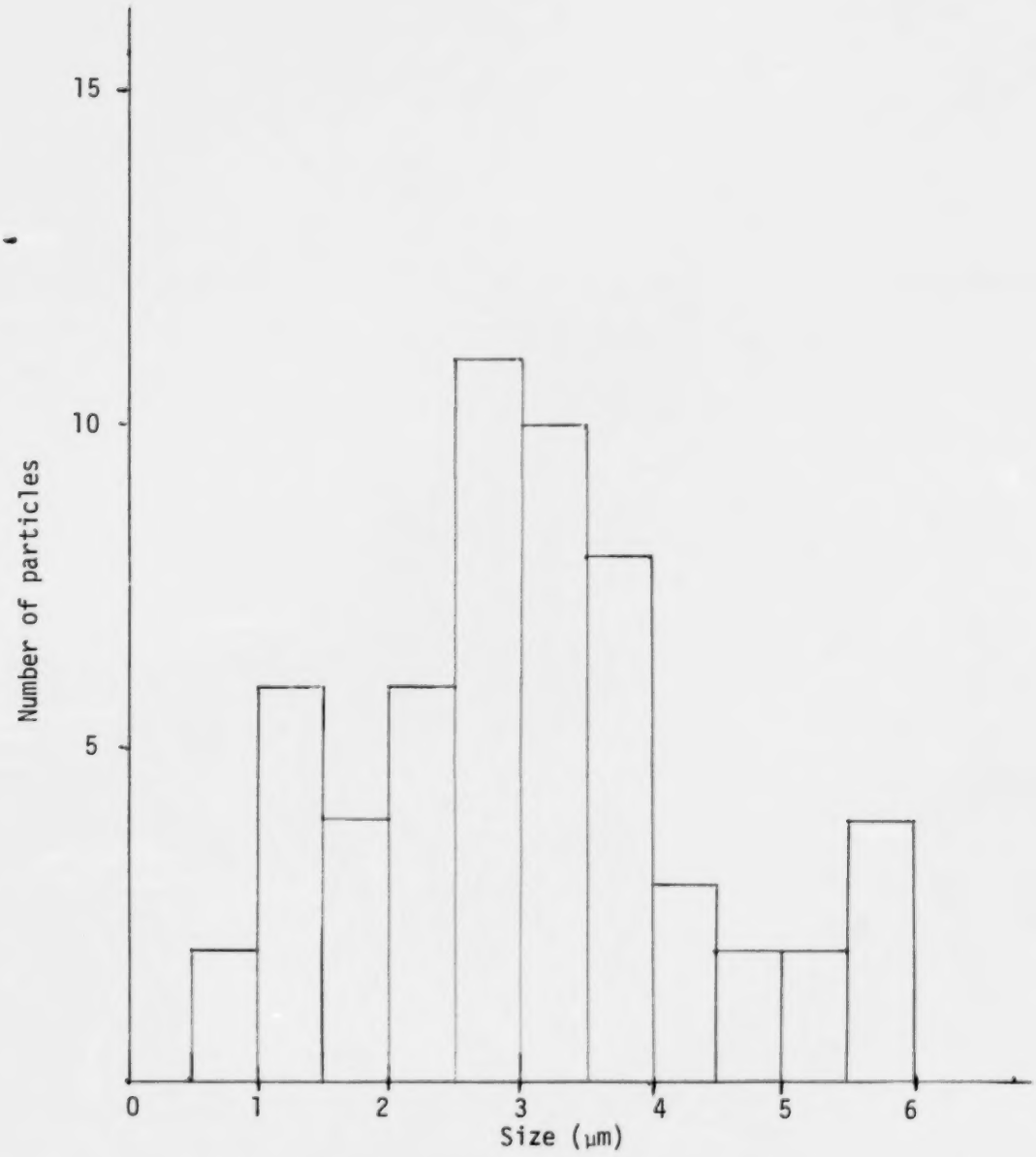


Figure 6. Results of SEM analysis of May 5 filter, background. Sample was taken outside the plume at 2:51 p.m. with a 0.4-μm filter; actual volume = 2.024 ft^3.

approximately 70% out of the plume due to tethered balloon control problems. The results shown in Figure 7 reflect this out-of-plume sampling, and over half the particles were pollen. Part of the particles were from the source as indicated by the elements Ca, Fe, Si, S, and Ti. As will be shown later, the source emitted particles were of similar composition. The pollen particles observed on these SEM filters were within a range from 40 to 80 μm.

Some confusion results from the analyses of the two remaining filters collected within the plume. The sample initiated at 3:06 p.m. showed more S and K than any other Nuclepore samples taken for SEM at this site. As shown in Figure 8, over 50% of the particles were between 0.2 and 0.4 μm and these showed a predominance of S and K. In fact, 69% of all particles showed S as either the major or minor element. These results are confirmed by the results of the $SO_3^=$ filter collected between 2:18 and 3:00 p.m., as shown in Table 4. Comparison of this $SO_3^=$ filter sample to all others collected, adjusted for sample volume, indicates the very high presence of $SO_3^=$ in the plume around 3:00 p.m. on the bypass mode day.

Figure 9 depicts the results of the Nuclepore sample initiated at 3:28 p.m. on the bypass day. Forty-three percent of the particles were spherical and contained Cl^- as a major constituent and were reactive to the electron beam. These particles were taken to be NH_4Cl and were predominantly between 0.2 and 1.2 μm. Another 44% of the total particles analyzed were mixtures of Cl, Ca, Si and Al. The remaining 13% were identified as pollen. This high level of chlorine was confirmed by similar results from the TFT filters, as indicated in Tables 1 and 2.

One interesting feature of the filter containing NH_4Cl is the result of a repeat analysis performed 23 days later on the same filter fraction which had been left exposed to laboratory air during the storage time. The repeat analysis showed no presence of spherical particles, but showed agglomerated

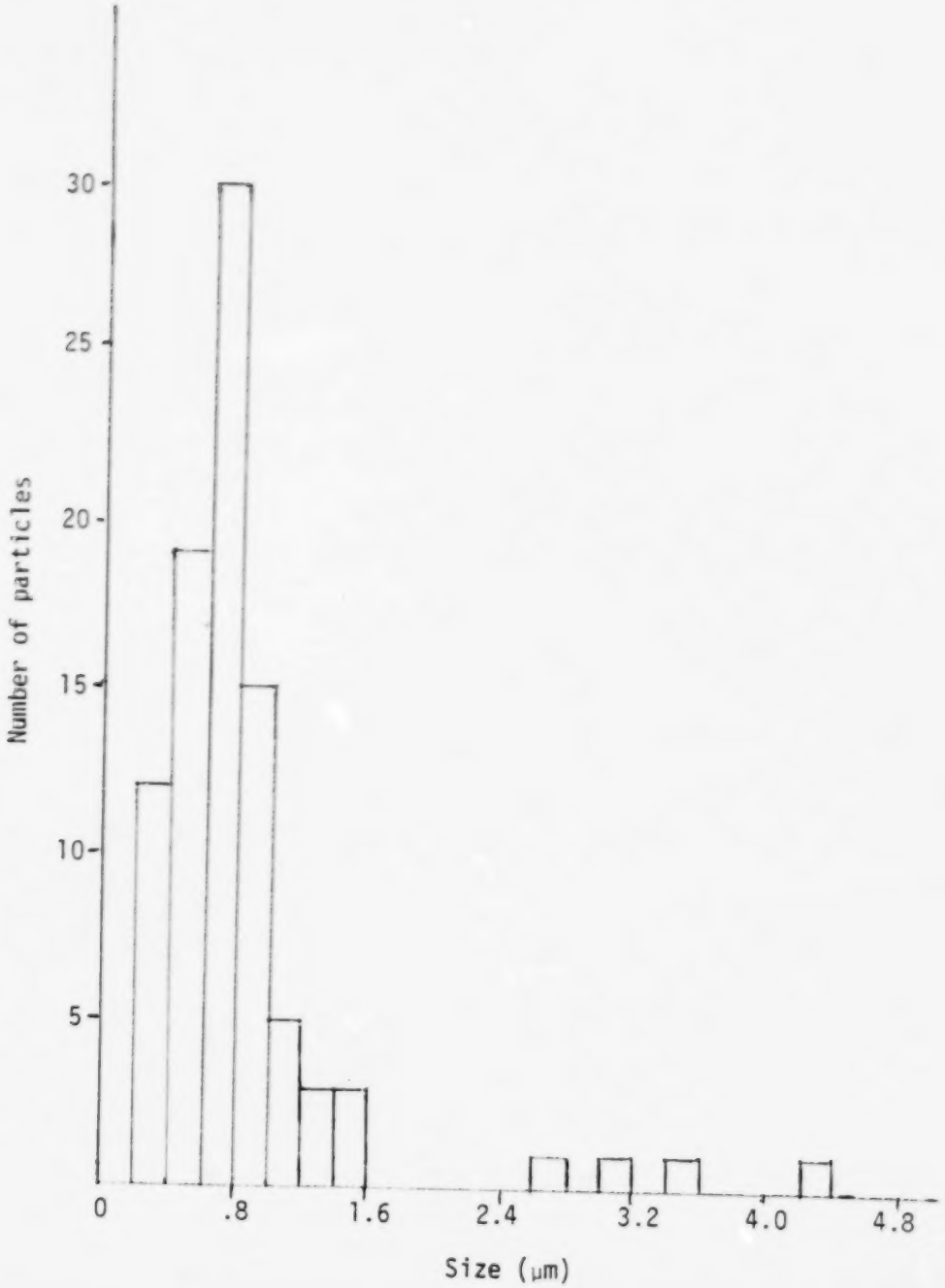


Figure 7. Results of SEM analysis of May 5 filter. Sample was taken at 11:25 a.m. with a 0.8-μm filter inside the plume; actual volume = 1.581 ft^3. Problems occurred with the tethered balloon control during collection of this sample.

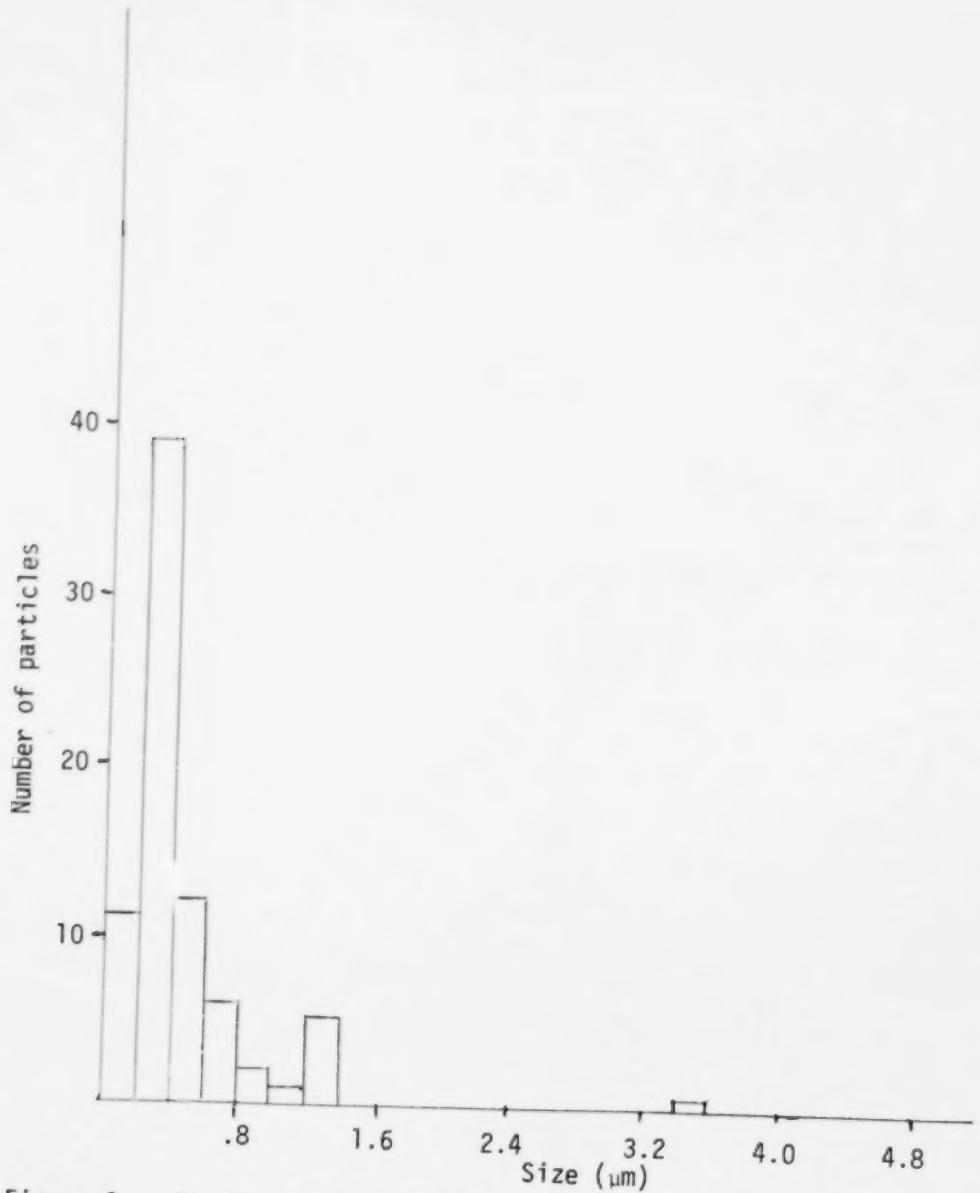


Figure 8. Results of SEM analysis of May 5 filter, in plume. Sample was taken at 3:06 p.m. with a 0.8-μm filter; actual volume = 1.596 ft^3.

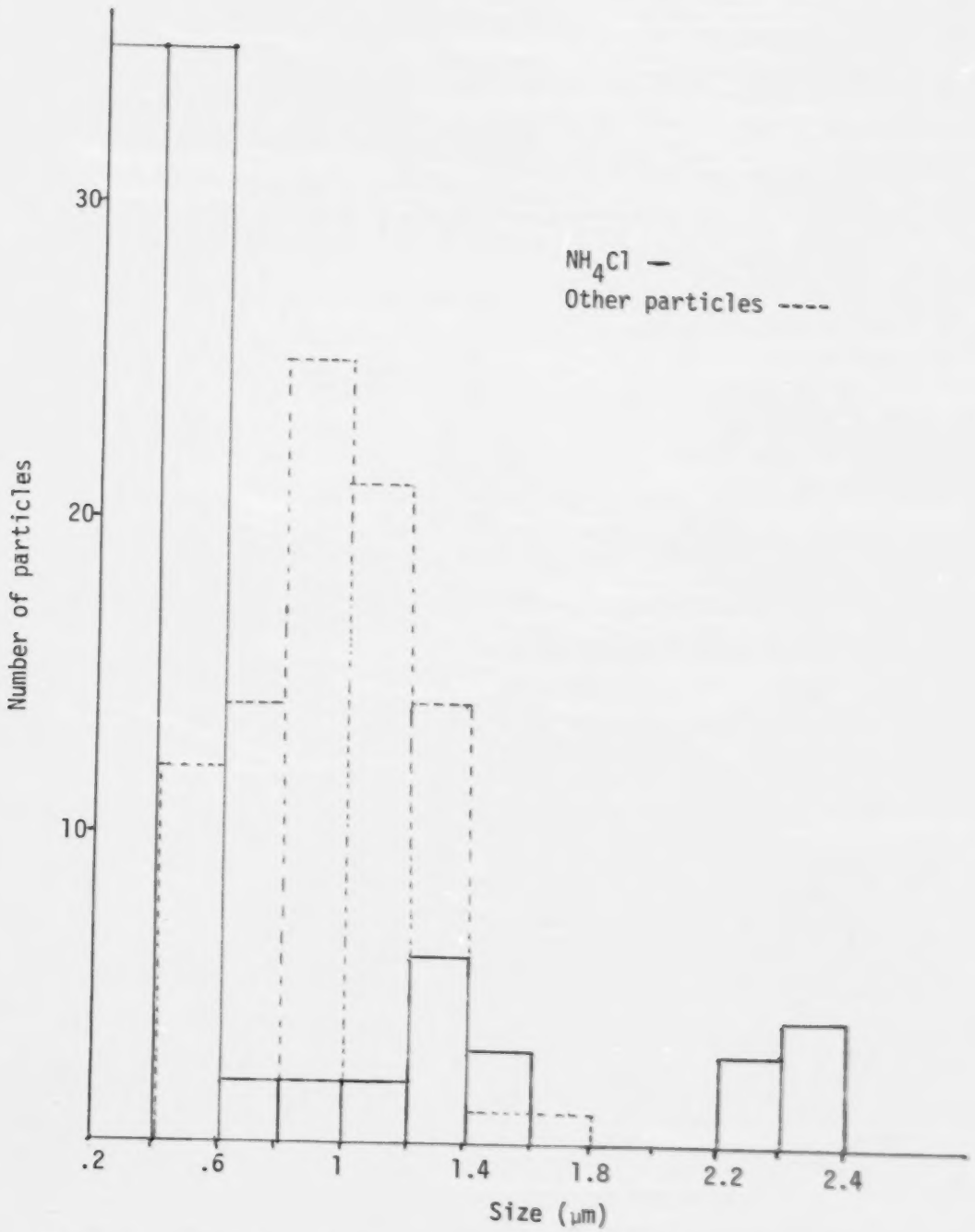


Figure 9. Results of SEM analysis of May 5 filter, in plume. Sample was taken at 3:28 p.m. with a 0.4-μm filter; actual volume = 2.047 ft^3.

massive areas of solid material containing Cl and Ca. These areas were non-reactive to the electron beam. It was assumed that, due to the hydroscopic nature of NH_4Cl, a liberation of the NH_3 had occurred from a reaction of NH_4Cl with Ca salts.

Sampling with Nuclepore filters for SEM analyses on Thursday, the mill mode day, produced no unexpected results. As shown in Figure 10, the in-plume sample from 12:28 to 1:38 p.m. consisted predominantly of 0.2- to 1.4-μm particles composed of Ca, Fe, and Si. Six percent of the particles were high in S content. The results of a simultaneous sample from the background are not shown, as the particles were all agglomerates of 1.5 to 15 μm. Again, the predominant elements were Ca, Fe, and Si. No particles were found to contain substantial amounts of sulfur. In-plume and background filters were collected during 4:49 to 4:59 p.m. on Thursday. Again, Ca, Si and Fe were the predominant elements in both samples. The presence of S in 10 and 9% of the particles for the in-plume and background samples indicates most of these sulfur-containing particles may be attributable to ambient air. As indicated in Figures 11 and 12, there is a slightly smaller size range for the in-plume particles (0.2 to 0.8 μm) than for the background particles (0.5 to 2.5 μm). For all Nuclepore samples within or as background to the plume, there was little Cl^- present except for the bypass mode in-plume samples. This is reasonably consistent with the TFT prefilters as analyzed by both IC and XRF. As will be discussed below, these results are also consistent with source emissions measurement results.

SOURCE MEASUREMENTS

Sampling Schedule

The complete schedule of source sampling, dictated by the operating schedule, weather, and limited working space on the stack, is shown in Table 6. As

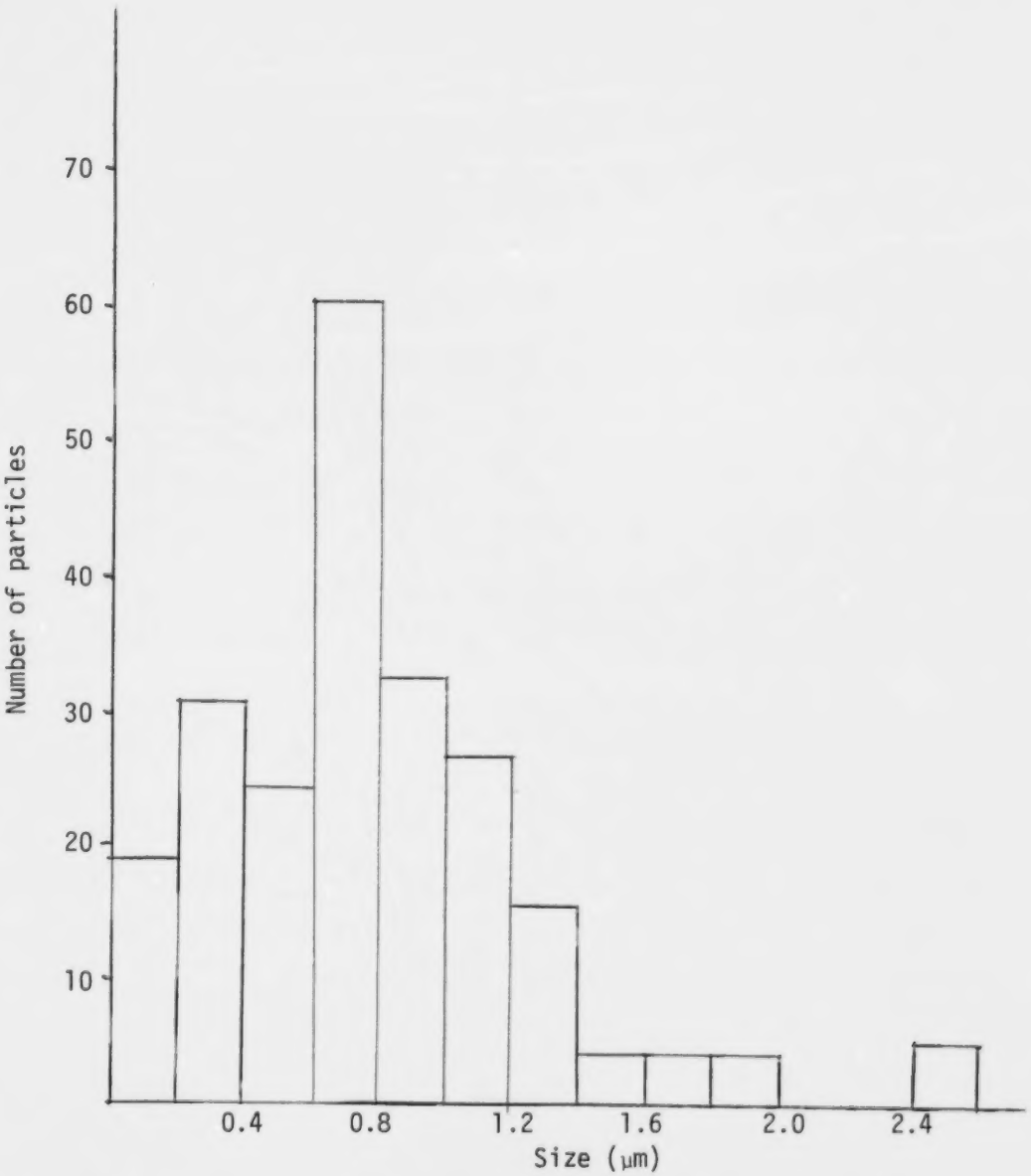


Figure 10. Results of SEM analysis of May 7 filter, in plume. Sample was taken at 12:28 p.m. with a 0.8-μm filter; actual volume = 7.046 ft^3.

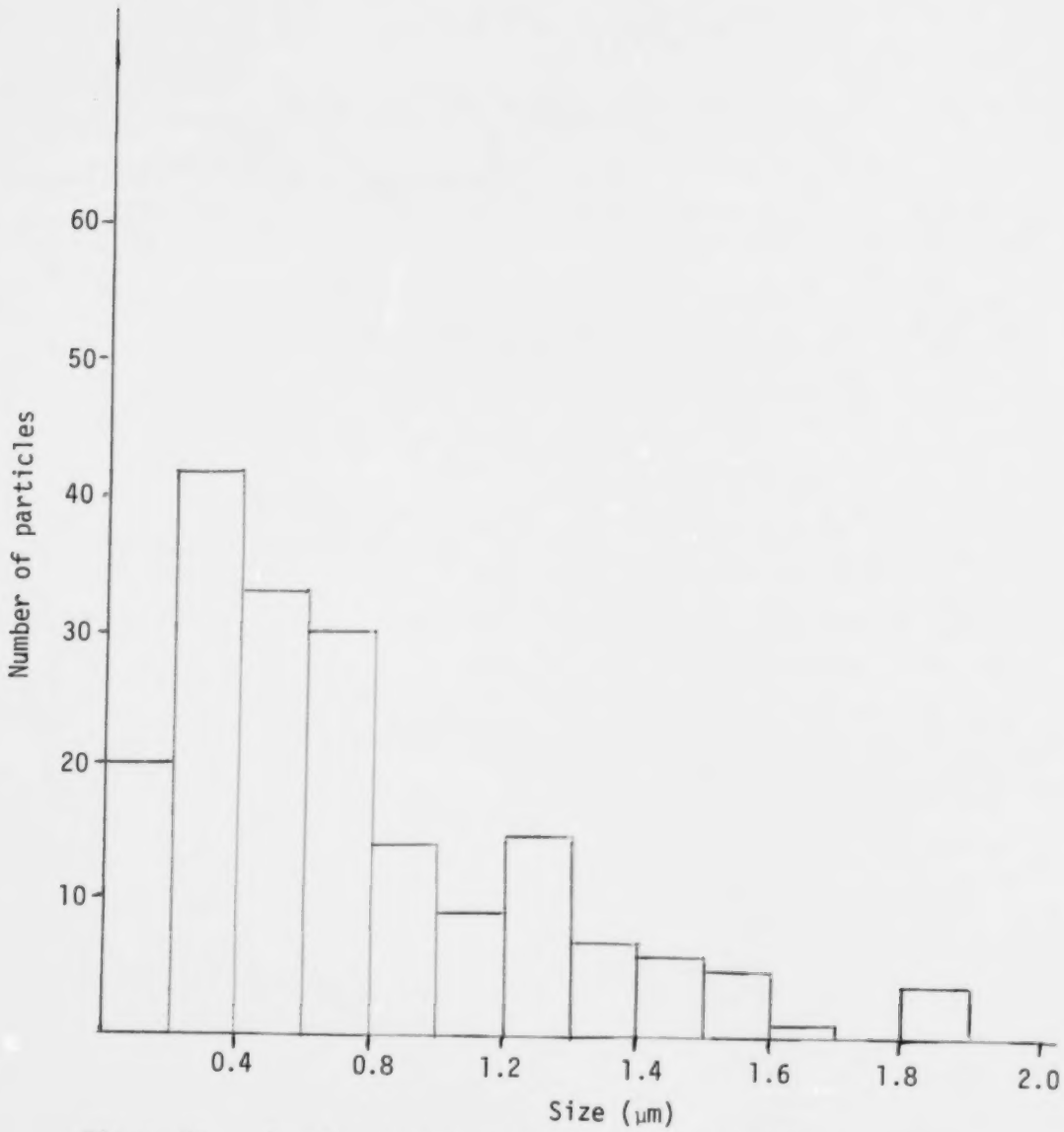


Figure 11. Results of SEM analysis of May 7 filter, in plume. Sample was taken at 4:49 p.m. with a 0.8-μm filter; actual volume = 7.922 ft^3.

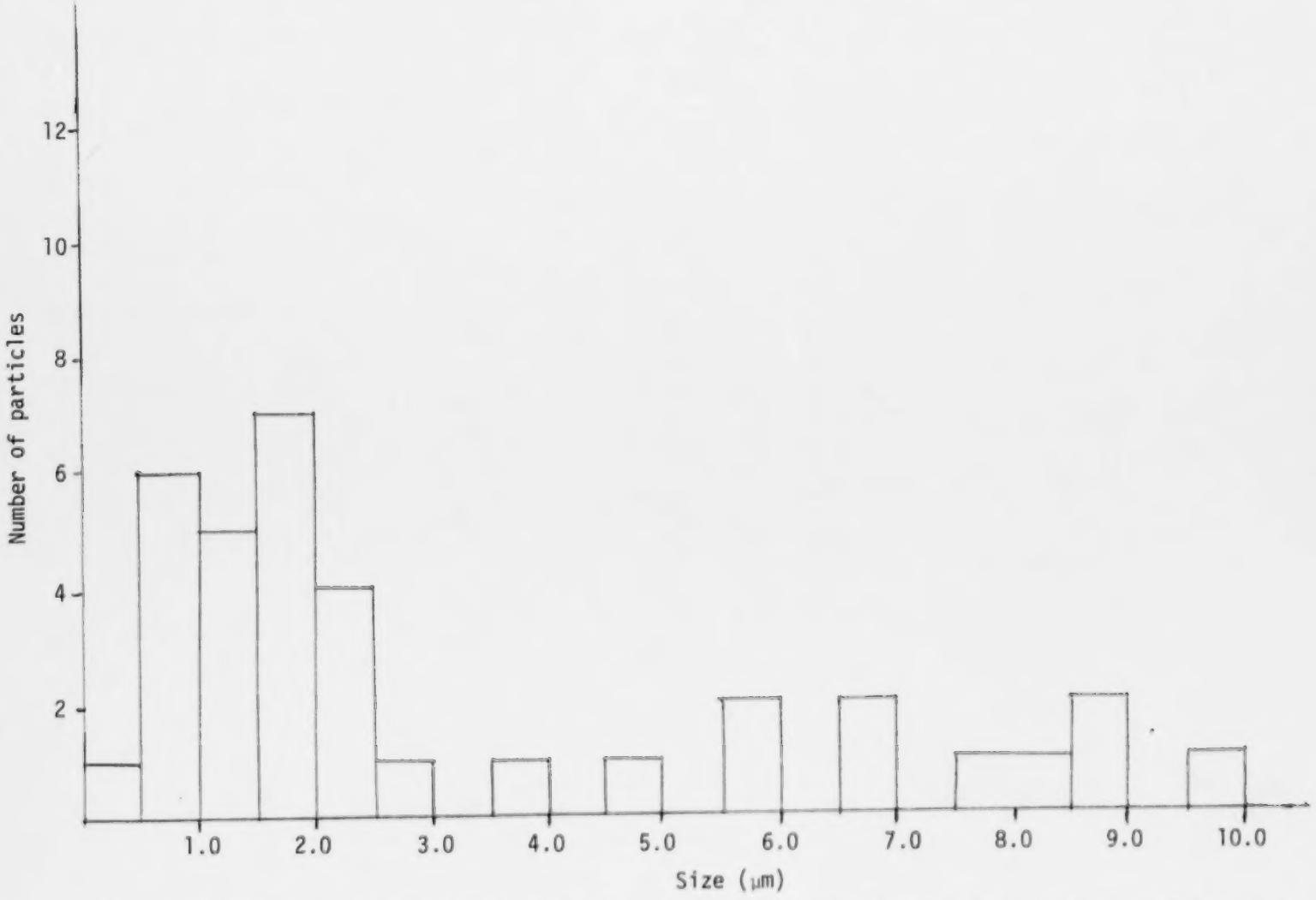


Figure 12. Results of SEM analysis of May 7 filter, background. Sample was taken at 4:49 p.m. with a 0.8-μm filter; actual volume = 8.397 ft^3.

TABLE 6. SCHEDULE OF SOURCE SAMPLING

Date	M-5	Pilat	Characterization	NO_x	NH_3, Cl^-, F^-	M-6	EPA-NH_3, HCl	ACS	ROSE	Mode
5/4	1726-1845	1722-1752	1532-1710	--	1635-1734	1824-1944	1622-1730	--	--	Mill
5/5	0957-1057	--	1023-1114	--	0826-0926	0826-0926	0819-NR	--	--	Bypass
5/5					1213-1313	1213-1313	0934-1019	--	--	Bypass
5/5							1233-1257	--	--	Bypass
5/5	1430-1530	1453-1508	--	--	1421-1521	1421-1521	1421-1516	--	1408	Bypass
5/5							1747-1821	--	1709	Mill
5/7	0935-1035	1041-1101	0937-1035	1002-1042	0938-1038	1037-1137	--			Mill
5/7	1215-1315	1222-1242	1119-1213	1330	1155-1255	1235-1335	--	1235-1310	--	Mill
5/7	1435-1535	1531-1551	1433-1522	1525-1600	1429-1529	1436-1536	--			Mill
5/8	--	--	--	--	--	--	--	0957-1041	--	Bypass

1. M-5 = EPA Standard Method 5
2. Characterization, using 6 types of filters
3. NO_x, NH_3, Cl^-, F^-, and M-6 are conventional methods and EPA Reference Methods 6 and 7
4. EPA-NH_3, Cl determined with MACS train
5. ACS = acid condensation measurement with MACS
6. ROSE is cross-stack optical FTIR method for gases

mentioned previously, methods addressing particulate loading and characterization were performed as nearly simultaneously as possible to provide comparison data. The same procedure was used for methods addressing gaseous sampling. Traverses were performed according to EPA Method 1 for both bypass mode and mill mode conditions, with the upstream disturbance conditions being met. The results of the traverses for ports A, B and C and their respective counterparts D, E and F across the stack are shown in Table 7. Subsequent calculations of mass emission rates utilized the results of these traverses and the measured velocity at the time of the measurement for each sampling point.

Gases

Conventional measurements of NH_3, Cl^-, F^-, SO_x, NO_x, CO_2, O_2, and H_2O were performed by the methods discussed earlier and according to the schedule in Table 6. Sampling for NH_3, Cl^-, SO_x, and H_2SO_4 was also performed with a version of a small acid condensation sampling train. The results of both NH_3 measurements are presented in Table 8. Because space and time were limited, NH_3 sampling with the EPA modified version was not conducted on Thursday. According to the conventional method, three measurements reflect an average of 16.3 ± 2.0 ppm of gaseous NH_3 during the bypass mode.

Five modified samples were taken on Tuesday; however, only three were taken as representative of the bypass mode. The initial sample, begun at 8:19 a.m., was not representative since the mode was switched at 8:00 a.m. and a stable condition had not been established. Three modified NH_3 tests were conducted from 9:34 a.m. to 3:16 p.m.; the average results of the three measurements was 17.9 ± 2.7 ppm of gaseous NH_3. This compares favorably with the average 16.3 ppm NH_3 obtained during the same sampling period by the conventional method. The average gaseous NH_3 concentration for the mill mode on Thursday was 2.4 ± 0.2 ppm.

TABLE 7. VELOCITY TRAVERSES FOR CEMENT PLANT STACK

5/5/81, Bypass Mode:

Reading point	Fraction of stack diameter	Distance[a] into stack	A (D) Vel. H[b]	A (D) °C	B (E) Vel. H	B (E) °C	C (F) Vel. H	C (F) °C
1	.098	211.4	1.10	117.2	1.10	122.2	1.00	119.4
2	.895	195.5	1.25	123.9	1.45	123.3	1.30	120.0
3	.806	176.1	1.40	126.7	1.55	124.4	1.45	121.1
4	.677	147.9	1.45	129.4	1.80	125.0	1.65	121.7
5	.323	70.6	.97	130.6	1.10	125.0	1.15	122.8
6	.194	42.4	.80	128.9	.87	125.0	1.05	122.8
7	.105	22.9	.65	128.9	.80	125.0	.97	122.8
8	.032	7.0	.60	128.3	.60	122.2	.80	122.8
		Port Averages:	1.03	126.7	1.16	124.0	1.17	121.7

Total Average: 1.12 Vel. H and 124.1°C

5/7/81, Mill Mode:

Reading point	Fraction of stack diameter	Distance[a] into stack	A (D) Vel. H[b]	A (D) °C	B (E) Vel. H	B (E) °C	C (F) Vel. H	C (F) °C
1	.968	211.4	1.85	82.8	2.10	85.6	2.50	86.1
2	.895	195.5	1.95	84.4	2.30	86.1	2.75	86.1
3	.806	176.1	2.00	84.4	2.65	86.1	3.15	86.7
4	.677	147.9	2.15	84.4	2.95	86.1	3.50	86.7
5	.323	70.6	2.25	85.6	2.00	86.1	1.85	86.7
6	.194	42.4	1.65	86.6	1.45	86.1	1.65	86.7
7	.105	22.9	1.35	85.0	1.25	86.1	1.65	86.7
8	.032	7.0	1.05	85.0	1.00	86.1	1.25	86.7
		Port Averages:	1.78	84.7	1.96	86.0	2.29	86.6

Total Average: 2.01 Vel. H and 85.8°C

a - Cm in from sampling port
b - Vel. H = Pitot tube manometer reading

TABLE 8. RESULTS OF NH_3 SAMPLING

Engineering Science NH_3

Date	Sample	Time	Probe plug (ppm)	Gaseous NH_3 (ppm)	Total NH_3 (ppm)	Gaseous NH_3 (%)
5/4/81	NH_3-1	1635-1734	.70	9.2	9.9	92.9
5/5/81	NH_3-2	0826-0926	5.2	17.3	22.5	76.9
5/5/81	NH_3-3	1213-1313	.6	19.1	19.7	96.9
5/5/81	NH_3-4	1421-1521	1.7	12.4	14.1	87.9
5/7/81	NH_3-5	0938-1038	1.1	2.6	3.7	70.3
5/7/81	NH_3-6	1155-1255	.4	--	.4	
5/7/81	NH_3-7	1429-1529	.4	2.2	2.6	84.6

EPA - NH_3

Date	Sample	Time	Probe plug filter (ppm)	Gaseous NH_3 (ppm)	Total NH_3 (ppm)	Gaseous NH_3 (%)
5/4/81	1-B	1622-1731	1.5	4.4	5.9	74.6
5/5/81	2-B	0819-unknown	29.6	7.4	37.0	20.0
5/5/81	3-B	0934-1019	4.1	13.9	18.0	77.2
5/5/81	4-B	1233-1257	4.4	21.4	25.8	82.9
5/5/81	5-B	1421-1516	13.3	18.5	31.8	58.2
5/5/81	6-B	1747-1821	1.5	7.6	9.1	83.5

Similar simultaneous sampling for gaseous HCl and total Cl^- was performed. The results of these measurements are shown in Table 9. Results from the conventional method indicate an average of 19.7 ppm of gaseous HCl was measured during the interval from 8:26 a.m. to 3:21 p.m. The 19.7 ppm average includes an extremely high 34.3 ppm HCl result from the 8:26 to 9:26 a.m. sample. For the two runs taken after temperature equilibrium had been reached, the average gaseous HCl was 12.4 ppm. A comparison of the four bypass samples for gaseous HCl obtained by the modified method gives an average concentration of 18.3 ppm. This higher value can be attributed to collection of a greater amount of the total HCl in the impingers when flat filters are used in the modified method in contrast to the glass probe plug in the conventional method.

The total NH_3 and Cl^- emissions measured by the two methods agree reasonably well if the two outliers are omitted. Disregarding the initial NH_3 run by the modified EPA method, which resulted in 29.6 ppm of particulate NH_3 on the probe plug, the average total NH_3 concentrations during the bypass mode was 25.2 ppm and 18.8 ppm for the EPA and conventional methods, respectively. Again disregarding the high HCl result by the conventional method, the total Cl^- for this same bypass mode was 23.9 ppm and 25.2 ppm by the EPA and conventional methods, respectively. The molar ratios of total NH_3 to total Cl^- were 1.06 and .75 according to the EPA and conventional measurements, respectively. These molar ratios do not compare well with the same total NH_3 to total Cl^- ratios of 0.61 and 1.7 for the TFT-11 and TFT-12 balloon filters, respectively.

Results of SO_x measurements for the two sampling modes are presented in Table 10. For the EPA Method 6 results for SO_2, all sulfate present in the sampling train beyond the probe plug is taken as derived from SO_2 in the stack. In the presence of NH_3, however, SO_2 is retained in the alcohol (IPA) impinger as sulfate. For this reason sulfate determinations were performed on the three

TABLE 9. RESULTS OF HCl SAMPLING

Engineering Science HCl

Date	Sample	Time	Probe plug (ppm)	Gaseous HCl (ppm)	Total HCl (ppm)	Gaseous HCl (%)
5/4/81	HCl-1	1635-1734	5.00	--	5.00	--
5/5/81	HCl-2	0826-0926	5.63	34.30	39.93	85.9
5/5/81	HCl-3	1213-1313	14.43	13.20	27.63	47.8
5/5/81	HCl-4	1421-1521	11.32	11.50	22.82	50.4
5/7/81	HCl-5	0938-1038	3.67	19.30	22.97	84.0
5/7/81	HCl-6	1155-1255	.34	6.31	6.65	94.9
5/7/81	HCl-7	1429-1529	2.85	13.01	15.86	82.0

EPA - HCl

Date	Sample	Time	Probe plug filter (ppm)	Gaseous HCl (ppm)	Total HCl (ppm)	Gaseous HCl (%)
5/4/81	1-A	1622-1730	.54	3.66	4.20	87.1
5/5/81	2-A	0751-0817	6.13	18.20	24.33	75.0
5/5/81	3-A	0932-1015	9.80	18.70	28.50	65.6
5/5/81	4-A	1222-1253	3.14	20.80	23.94	86.7
5/5/81	5-A	1422-1513	3.84	14.90	18.74	79.4
5/5/81	6-A	1747-1821	.98	1.58	2.56	61.7

TABLE 10. RESULTS OF TOTAL SULFATE ANALYSIS OF SO_x SAMPLES

Method 6

Date	Sample	Volume[a] ft^3	Probe plug (ppm)	Probe wash plus IPA (ppm)	H_2O_2 (ppm)	Total SO_2 (ppm)	O_2 (%)
5/5	M-6	1.707	2.25	148.60	1.46	150	9.7
5/5	M-6	1.658	2.26	13.79	67.31	81.1	9.7
5/5	M-6	1.870	3.66	44.46	11.11	55.6	11.5
5/7	M-6	1.746	3.05	3.79	6.39	10.18	13.9
5/7	M-6	1.801	1.98	5.76	3.98	9.74	14.4
5/7	M-6	1.686	2.44	3.21	4.53	7.74	14.2

Acid Condensation:

Date	Sample	Volume	Probe wash (ppm)	Filter (ppm)	Glass plug (ppm)	H_2O_2 (ppm)
5/7	MACS	1.40	0.22	0.15	0.27	11.47
5/7	MACS	1.56	0.09	0.18	0.22	10.98
5/8	MACS	1.44	0.22	0.14	1.20	25.53
5/8	MACS	1.59	0.16	0.16	1.14	37.99

a - Sample Volumes corrected to cu. ft. at STP.

separate fractions of probe plug (PP) taken as particulate sulfate and sulfuric acid, probe wash combined with the IPA impinger catch, and the peroxide (H_2O_2) catch. The results of the conventional Method 6 for SO_2 are highly inconsistent. Results from the initial sample, taken on Tuesday from 8:26 to 9:26 a.m., during the period of instability when the mill mode was changed to the bypass mode, were disregarded in interpreting the data. The average of the remaining two results (81.1 and 55.6 ppm SO_2) is 68.4 ppm SO_2. Better agreement is seen when a correction is made for the difference in the O_2 levels during sampling. Correcting the 9.7% O_2 result of 81.1 ppm SO_2 to the 11.5% level gives a revised SO_2 concentration of 68.2 ppm, and the resulting SO_2 average would be 61.9 ppm. This is a higher SO_2 concentration for the bypass mode than that measured by the acid condensation system sampling on Friday, also shown in Table 10. The SO_2 concentration average of these two measurements (25.5 and 38.0 ppm) is 31.7 ppm; however, no O_2 measurements were taken on Friday, so a comparison of the 31.7 ppm SO_2 by the MACS method to the conventional measurement result of 61.9 ppm SO_2 for the bypass mode is questionable. Agreement between the SO_2 measured by the two methods on Thursday is much better, with average results of 9.22 and 11.2 ppm SO_2 according to the MACS and Method 6 procedures, respectively. Again, no O_2 concentrations were measured at the MACS point of sampling, but, unlike the bypass mode, for which SO_2 results acquired on separate days were compared, all mill mode sampling by the two methods was on Thursday.

As indicated in Table 10, according to the ACS sampling results only 0.25 ppm of H_2SO_4 was collected on the glass plug on Thursday during the mill mode, in contrast to the 1.17 ppm collected on Friday during the bypass mode. Calculation of the molar amount of H_2SO_4 emitted from the source in the bypass mode relative to that of NH_3 gives an NH_3:H_2SO_4 ratio of 20.4. From this ratio

and assuming that all other sulfur passed as SO_2 gas through the TFT filters, the indication is that a negligible amount of SO_x reacts with NH_3.

In the conventional HCl sampling train catch, samples were screened for F^- in addition to Cl^-. These results and the limited NO_x, CO_2 and O_2 measurements are presented in Table 11. As indicated in the table, there was little F^- present in the source emissions.

Table 12 presents the results of the measurement of selected gases by the FTIR ROSE system. Several of the manual gas measurement methods were conducted simultaneously with the optical method. The 11, 15 and 40 ppm of NH_3, HCl, and SO_2, respectively, measured by the ROSE system are in fair agreement with the results from manual methods taken during the bypass mode, but are lower than the average manual method results of 18, 18, and 62 ppm for NH_3, HCl, and SO_2, respectively. Nearly equivalent results were obtained for HCl in this mode by all methods. A second measurement at a longer wavelength by the ROSE system for SO_2 resulted in a measured concentration of 57 ppm which compares more favorably with the extractive method results. For the mill mode, the NH_3 concentration of 3 ppm compares well with the average 2.4 ppm NH_3 acquired by the conventional method on Thursday, but does not compare well with the 7.6 ppm NH_3 as measured by the EPA modified method conducted simultaneously. The HCl concentration of <0.5 ppm is comparable to the EPA modified method for HCl, which yielded 1.6 ppm HCl. The conventional gaseous HCl, as measured on Thursday in the mill mode, averaged 12.9 ppm, which was higher than that measured by the ROSE system.

A summary of the mass emission rates of NH_3, Cl^-, F^-, and SO_2 is presented in Table 13. Also included are the moisture concentrations (as determined by gravimetric determination of the Method 5 impinger catch) and the CO_2 and O_2 results. Also shown are the gas flow rates used to calculate the mass emission rates for the measured gases, which were extracted from different locations in

TABLE 11. RESULTS OF OTHER GASEOUS MEASUREMENTS

Date	Time	Method	F^{-} (a)	NO_x (a)	CO_2 (b)	O_2 (b)
5/4	1635 - 1734	M-6	0.91	--	8.8	18.2
5/5	0826 - 0926	M-6	0.34	--	18.2	9.7
5/5	1213 - 1313	M-6	0.22	--	--	--
5/5	1421 - 1521	M-6	0.15	--	16.5	11.9
5/7	0938 - 1038	M-6	0.23		11.5	13.9
5/7	1002 - 1042	M-7		191,211,281		
5/7	1155 - 1255	M-6	0.79		10.6	14.4
5/7	1330 - --	M-7		384		
5/7	1429 - 1529	M-6	0.26		11.3	14.2
5/7	1525 - 1600	M-7		332,294,271		

(a) PPM (v/v)
(b) % by volume

TABLE 12. RESULTS OF ROSE OPTICAL MEASUREMENTS[a]

Species	Time	Bypass mode	Time	Mill mode
HCl	1408	15	1814	< .5
NH_3	1709	11	1755	3
SO_2 (S)[b]	1408	40	1814	<10
SO_2 (L)[b]	1709	57	1755	27
CO	1408	70	1814	74
CO_2	1408	12.6%	1814	11.5%
NO	1408	385	1814	421

a - PPM (v/v), unless otherwise indicated, at stack conditions
b - SO_2 (S) and SO_2 (L) indicates SO_2 measured by short and long wavelength, respectively

TABLE 13. MASS EMISSION RATES FOR CONVENTIONALLY MEASURED COMPOUNDS

Date	Stack gas[1] flow rate (M-5)	Particulate		% H_2O[2]	Stack gas[3] flow rate (G)	NH_3		HCl		F^-		SO_2		Orsat		M[4]
		Gr/SCF	lb/hr			ppm	lb/hr	ppm	lb/hr	ppm	lb/hr	ppm	lb/hr	CO_2	O_2	O_2
5/4	143,119	0.012	14.33	13.07	142,920	9.85	3.74	4.98	3.74	0.91	0.39	13.80	19.82	8.8	18.2	13.5
5/5	97,490	0.011	15.43	15.25	98,461	22.53	5.88	39.92	22.34	0.34	0.10	150.0	146.0	18.2	9.7	10.0
5/5	--	--	--	--	98,858	19.64	5.15	27.64	15.54	0.22	0.07	81.1	79.9	--	--	--
5/5	111,734	0.005	7.66	16.23	98,414	14.13	3.69	22.82	12.77	0.15	0.04	55.6	53.8	16.5	11.9	10.5
5/7	144,621	0.005	8.50	13.36	146,038	3.66	1.42	22.94	19.05	0.23	0.10	10.18	14.8	11.5	13.9	13.8
5/7	144,763	0.005	8.52	13.46	146,409	0.35	0.14	6.64	5.53	0.79	0.34	9.74	14.2	10.6	14.4	13.8
5/7	144,410	0.005	9.23	13.51	145,929	2.66	1.03	15.86	13.16	0.26	0.11	7.74	11.3	11.3	14.2	14.2

(1) Volumetric flow rate from Method 5 pitot tube readings, scf/m

(2) % H_2O as determined from increase in H_2O in the impingers of M-5

(3) For gaseous sampling based on the sampling point and the velocity according to the traverse, scf/m

(4) Determined by a continuous reading MSA oxygen monitor

the stack than the particulates. The mass emission rates of particulate matter, measured according to the EPA Method 5 procedure, are presented in Table 14 along with the appropriate gas flow rates. Comparisons of the various particulate measurements will be presented in the next section.

Particles

Source sampling for particle loading, sizing, and composition was conducted by Standard Reference Method 5, Pilat impactors, and a series of characterization filters as described in the Experimental Section and Table 6. Due to the unfortunate scheduling of the bypass mode, only a few samples were acquired in that mode. The results from the mass loadings according to the Reference Method 5 and from the Pilat impactors, are presented in Table 14. The average emission rate for the mill mode measured by Pilat was 7.2 lb/hr as compared to 8.7 lb/hr measured by Method 5. The mass emission rates for the bypass mode are highly inconsistent and difficult to interpret. The earliest Method 5 emission rate was twice that of the afternoon sample. The Pilat emission rate for one sample was 18.3 lb/hr; at the same time the Method 5 sample gave a rate of 7.7 lb/hr.

The results showing the particle size distribution from the Pilat impactor are presented in Figures 13 through 17. Figure 13 shows the single bypass sample without the filter and indicates a maximum in the particle size distribution of about 2 μm diameter. Figure 14 shows the same sample, but includes the filter catch. The filter catch represents 56.3% of the total mass collected for this sample and indicates a predominance of particles with diameters below 0.4 μm.

For the mill mode, Pilat Samples 5, 6, and 7 were collected on Thursday and the results are presented in Figure 15. All three samples are consistent in pattern and differ from Sample 2 with respect to the filter catch. In the mill mode, the filter catch represents an average of only 17.9% of the total

TABLE 14. RESULTS OF PARTICULATE SAMPLING AT A CEMENT PLANT

PILAT

Date	Time	Velocity (m/s)	Emission Rate (Kg/hr)	Mass Concentration (mg/m^3)	Pilat Filter	
					(mg/m^3)	%
5/4	17:22-17:52	31.9	5.81	20.54	4.08	19.9
5/5	14:53-15:08	30.2	8.30	37.06	20.90	56.3
5/7	10:41-11:01	30.7	3.18	11.69	2.79	23.9
5/7	12:22-12:42	30.7	3.04	11.12	1.89	17.0
5/7	15:31-15:51	30.7	3.58	13.14	1.70	12.9

METHOD 5 (Front Half)

Date	Time	Velocity (m/s)	Emission Rate (Kg/hr)	Mass Concentration (mg/m^3)	H_2O (%)
5/4	17:26-18:45	26.3	6.49	27.4	13.1
5/5	9:57-10:57	20.9	6.99	41.2	15.2
5/5	14:30-15:30	24.4	3.49	18.3	16.2
5/7	9:35-10:35	26.6	3.86	16.0	13.4
5/7	12:15-13:15	26.6	3.86	16.0	13.4
5/7	14:35-15:35	26.6	4.17	16.0	13.5

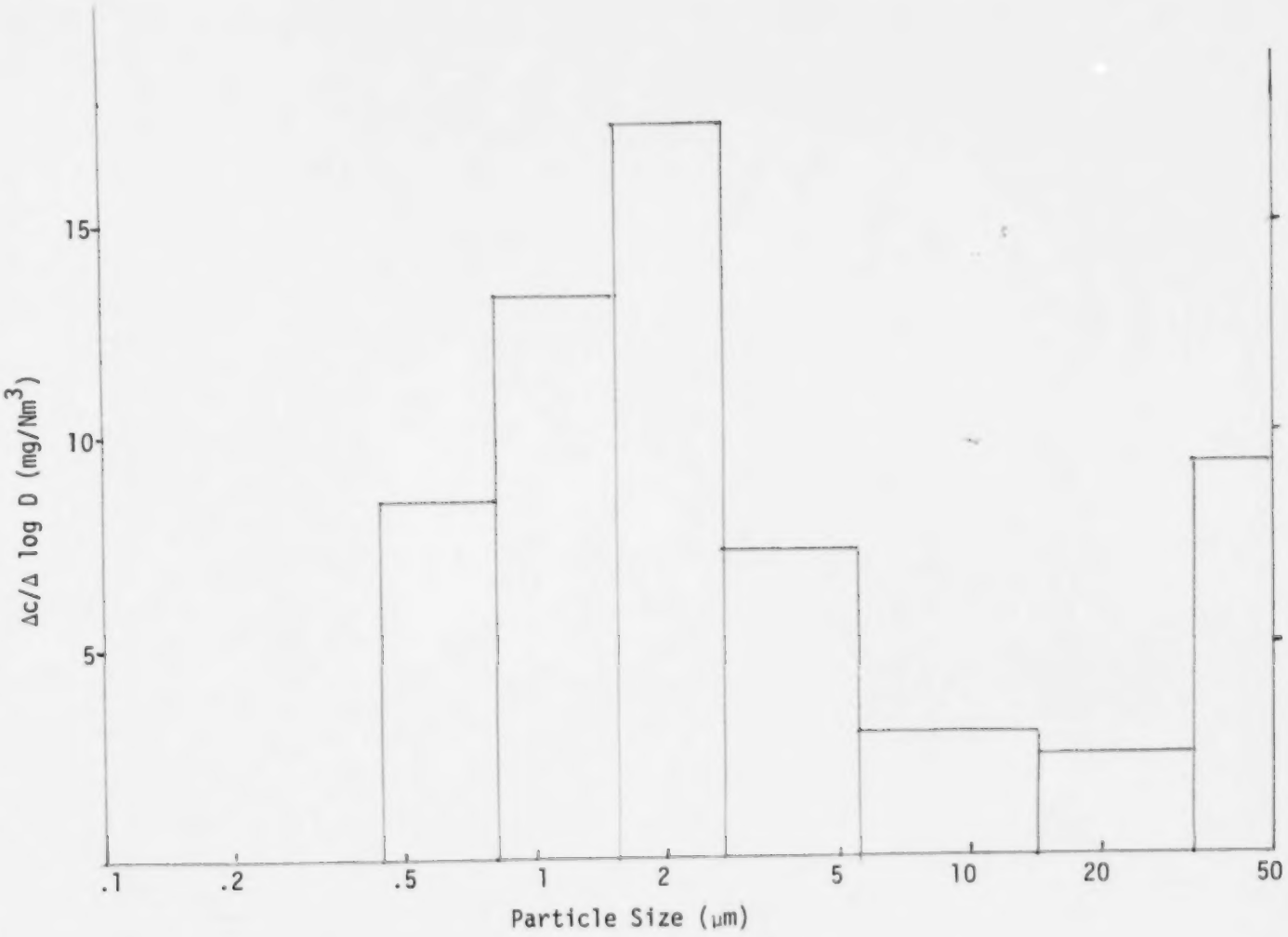


Figure 13. Distribution for Pilat run No. 2 (no filter).

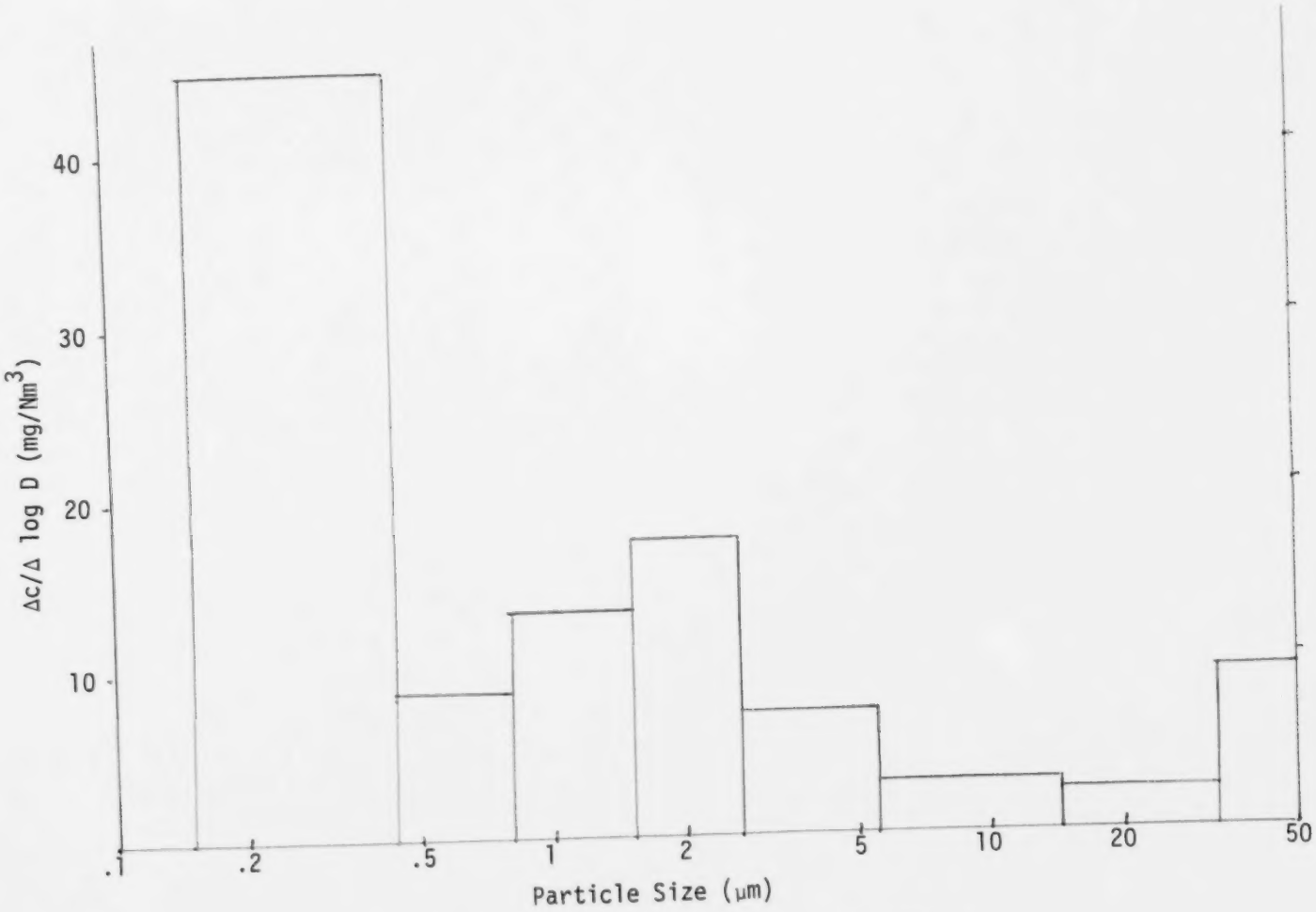


Figure 14. Distribution for Pilat run No. 2 (with filter)

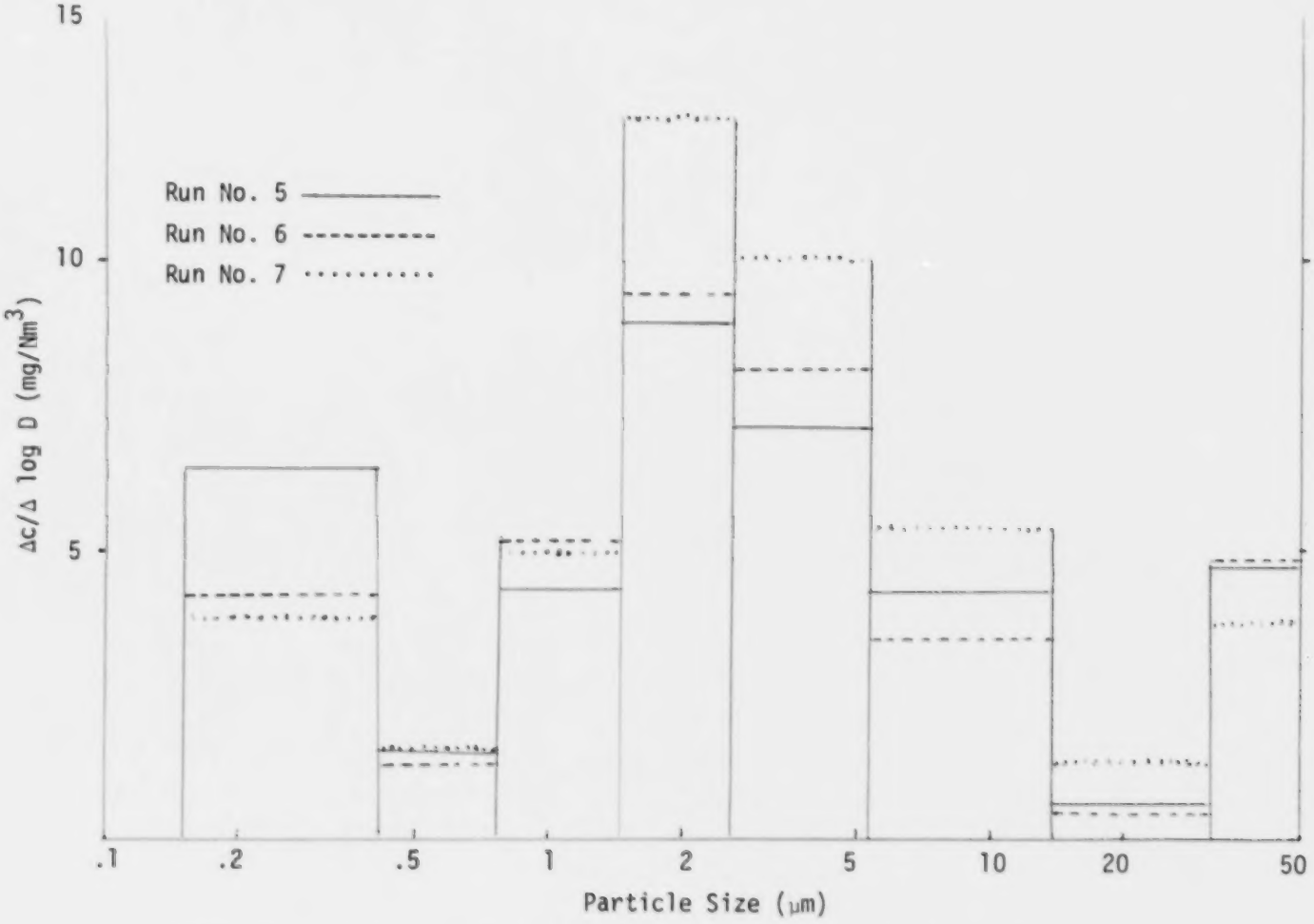


Figure 15. Distribution for Pilat runs No. 5, 6, 7 (with filters).

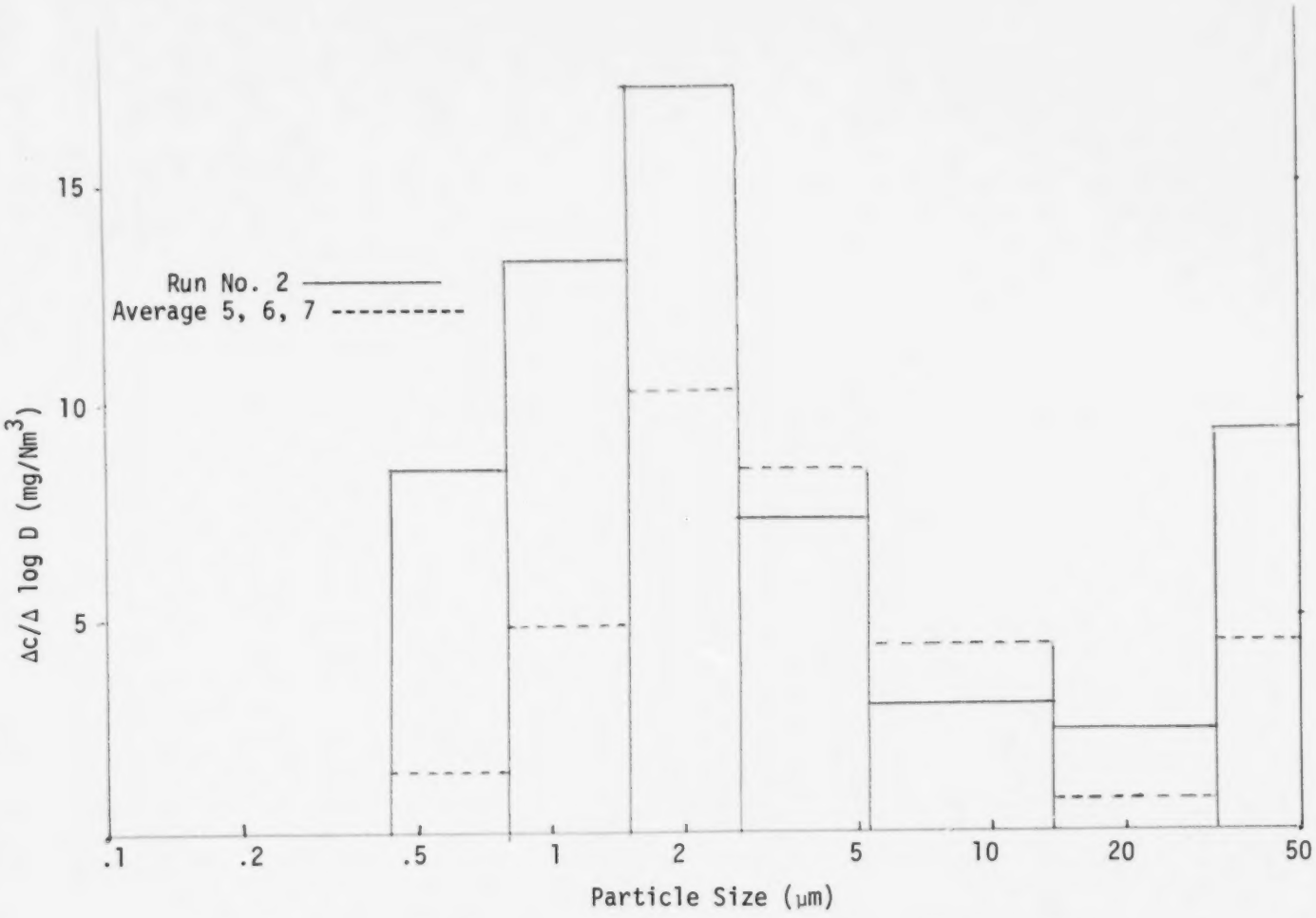


Figure 16. Distribution for Pilat runs No. 2 and 5, 6, 7 average (no filter)

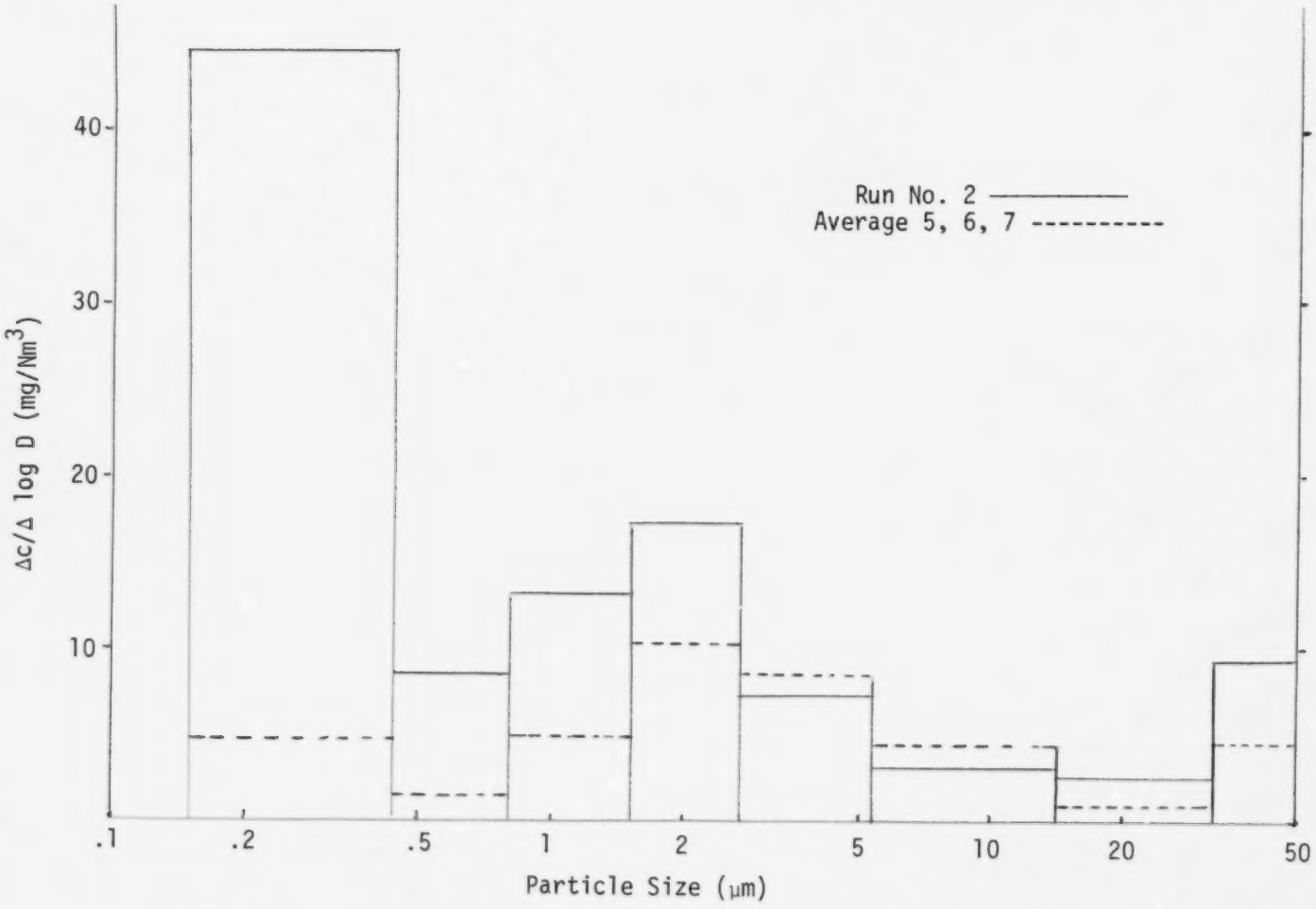


Figure 17. Distribution for Pilat runs No. 2 and 5, 6, and 7 average (with filter)

mass collected. Figure 16 shows the average distribution for Samples 5, 6 and 7 and the distribution of Sample 2 with no filter catch. It is obvious that the size distribution throughout the impactors is similar but with both smaller particles and greater loading in the bypass mode.

Figure 17 shows the particle size distribution for the average of Samples 5, 6, and 7 and the Sample 2 catch, including the filter catches. The figure shows the dramatic and dominant presence of small particles in Sample 2, representing the bypass mode emissions. The distribution of particle sizes, including the filter catch for the bypass mode and the average of the three samples for the mill mode, is shown in Figure 18.

After the impactor plates were weighed, the sized particle fractions were transferred by sonic removal with pentane to polycarbonate films for XRF analysis. Tables 15 through 20 show the results of XRF analyses for the individual impactor plates of each Pilat sample. The presence of the most abundant elements is consistent with the XRF analysis of the TFT filters for all mill mode samples. For the Pilat 2 sample, taken during the bypass mode, the third most abundant element was Cl. This total (1313 $\mu g/Nm^3$) shown in Table 16 is due in large part to the 1004 $\mu g/Nm^3$ on the filter. Without the filter catch, Cl would be the seventh most abundant element, comparable to its presence in the mill mode catches. A reasonable explanation for this result is the collection of Cl as gaseous HCl by the filter and particles collected on the filters. Laboratory experience has shown that glass filters, along with particles from coal-fired and refuse-fired burners can act as gaseous HCl collectors.

A series of five particulate characterization samples was acquired during the study. The average results of the XRF analyses of the six types of filters are shown in Tables 21 through 25. Quite consistent with the Pilat fractions, the same most abundant elements are detected for the mill mode samples. The results for the bypass mode, shown in Table 22, indicate an increase in Cl.

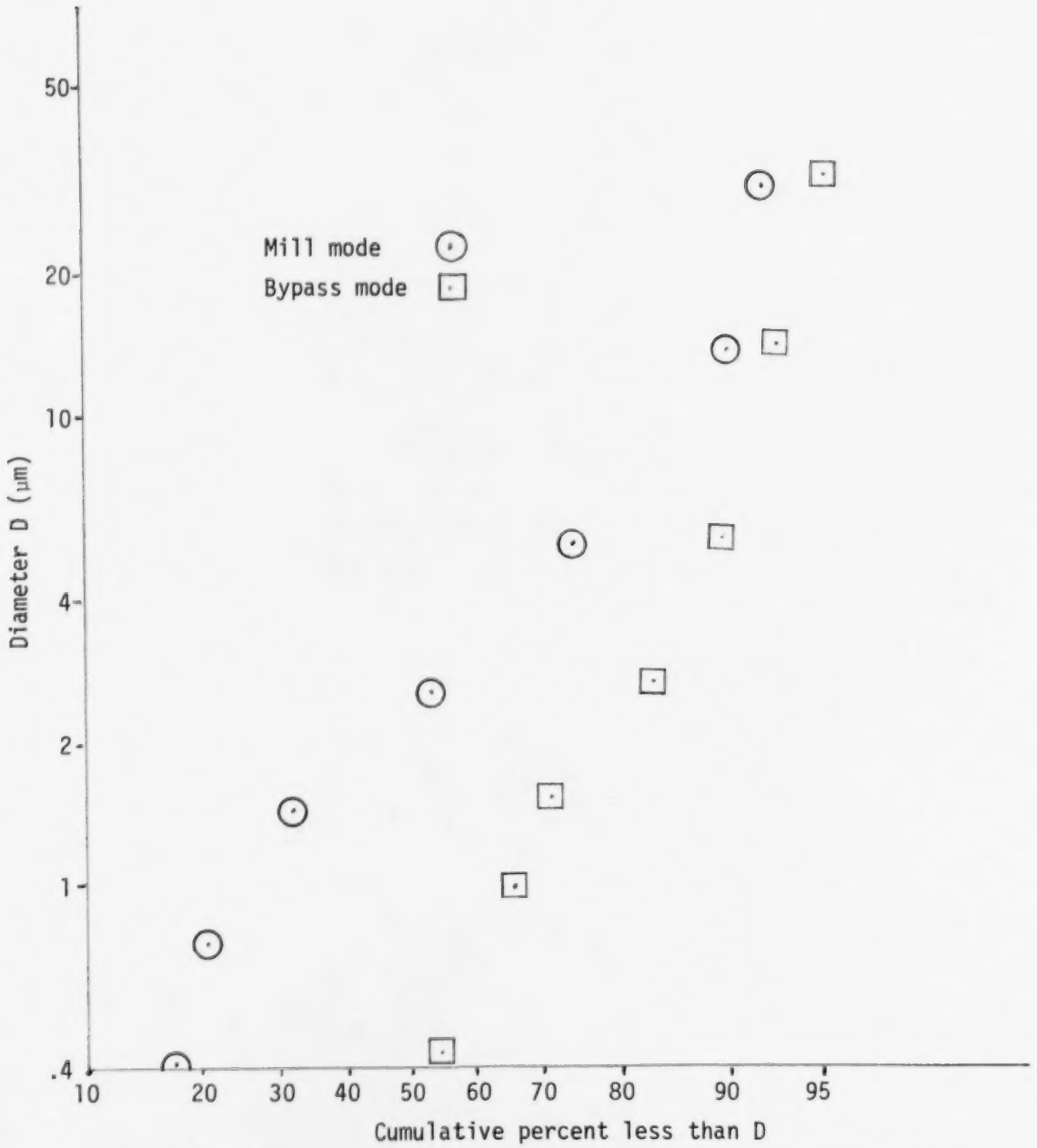


Figure 18. Comparison of Pilat results for bypass and mill modes.

TABLE 15. RESULTS[a] OF XRF ANALYSIS OF PILAT SAMPLE NO. 1

Date: 5/4/81 Time[b]: 1722 hrs. Volume: .3478 DNCM Mass Emission Rate[c]: 5.806 Kg/Hr

Stage	Size (μm)	Ca	Si	Fe	S	Al	Cl	K	Mg	Sn	Ti
1	50-30	114	43	158	19	5	--	3	2	2	1
2	30-15	95	110	59	26	4	--	3	2	1	1
3	15-5	512	99	63	34	22	13	13	6	7	3
4	5-3	828	142	59	47	43	19	25	10	12	7
5	3-1.5	591	201	51	28	51	--	23	11	9	7
6	1.5-.73	394	114	51	18	43	--	17	9	6	7
7	.73-.38	106	67	34	15	11	--	4	3	2	2
Filter	<.38	--	--	71	60	--	111	--	--	--	2
Total		2640	776	546	247	179	143	88	43	39	30

(a) $\mu g/Nm^3$ for the ten most abundant elements detected
(b) Time run was initiated
(c) Based on total Pilat catch

TABLE 16. RESULTS[a] OF XRF ANALYSIS OF PILAT SAMPLE NO. 2

Date: 5/5/81 Time[b]: 1453 hrs. Volume: .1319 DNCM Mass Emission Rate[c]: 8.292 Kg/Hr

Stage	Size (μm)	Ca	Si	Cl	K	Fe	S	Al	Mg	Ti	Sn
1	50-33	78	177	--	11	29	72	24	6	3	--
2	33-15	--	125	--	--	53	21	16	4	--	--
3	15-5.5	322	196	63	27	47	74	42	9	3	3
4	5.5-2.7	520	197	--	34	46	61	51	11	5	8
5	2.7-1.6	1143	312	38	96	100	89	104	24	16	20
6	1.6-.81	1039	447	94	229	125	125	125	25	20	15
7	.81-.44	239	187	114	333	82	146	51	9	5	3
Filter	<.44	--	--	1004	55	293	146	--	--	2	--
Total		3341	1641	1313	785	775	734	413	88	54	49

(a) $\mu g/Nm^3$ for the ten most abundant elements detected
(b) Time run was initiated
(c) Based on total Pilat catch

TABLE 17. RESULTS[a] OF XRF ANALYSIS OF PILAT SAMPLE NO. 3

Date: 5/6/81 Time[b]: 1725 hrs. Volume: .2133 DNCM Mass Emission Rate[c]: 10.529 Kg/Hr

Stage	Size (μm)	Fe	Ca	Si	S	Al	Cl	Zn	K	Mn	Br
1	50-32	122	174	53	45	8	--	--	5	3	--
2	32-15	50	135	161	38	10	--	--	4	2	--
3	15-5.3	58	707	141	54	29	--	--	17	--	--
4	5.3-2.6	77	964	289	64	50	--	--	28	--	--
5	2.6-1.5	71	643	257	55	57	--	--	30	--	--
6	1.5-.77	59	219	193	40	30	--	--	13	3	--
7	.77-.42	37	84	116	29	12	--	21	5	--	--
Filter	<.42	3105	--	--	116	--	168	142	5	59	65
Total		3579	2926	1210	441	196	168	163	102	67	65

(a) $\mu g/Nm^3$ for the ten most abundant elements detected
(b) Time run was initiated
(c) Based on total Pilat catch

TABLE 18. RESULTS[a] OF XRF ANALYSIS OF PILAT SAMPLE NO. 5

Date: 5/7/81 Time[b]: 1041 hrs. Volume: .2111 DNCM Mass Emission Rate[c]: 3.191 Kg/Hr

Stage	Size (μm)	Si	Ca	Fe	S	Cl	Al	Na	K	Mg	Cr
1	50-32	117	130	227	40	--	6	5	4	3	10
2	32-15	409	136	71	46	21	8	10	5	4	8
3	15-5.2	149	234	42	23	--	12	14	5	5	5
4	5.2-2.7	448	714	78	71	29	35	10	19	12	12
5	2.7-1.5	364	338	53	50	19	27	19	12	8	--
6	1.5-.76	104	110	25	31	23	14	4	6	3	--
7	.76-.42	156	78	31	28	21	7	--	3	3	1
Filter	<.42	--	--	8	26	63	--	--	--	--	--
Total		1747	1740	535	315	176	109	62	54	38	36

(a) $\mu g/Nm^3$ for the ten most abundant elements detected
(b) Time run was initiated
(c) Based on total Pilat catch

TABLE 19. RESULTS[a] OF XRF ANALYSIS OF PILAT SAMPLE NO. 6

Date: 5/7/81 Time[b]: 1222 hrs. Volume: .2087 DNCM Mass Emission Rate[c]: 3.044 Kg/Hr

Stage	Size (μm)	Ca	Fe	Si	S	Al	K	Na	Mg	Ti	Sn
1	50-32	65	131	17	26	3	3	7	1	2	1
2	32-15	--	47	16	11	--	--	5	--	--	--
3	15-5.4	263	59	48	16	12	7	--	4	2	3
4	5.4-2.7	499	62	79	27	32	13	--	7	4	7
5	2.7-1.5	414	43	99	24	34	14	12	7	5	5
6	1.5-.77	256	40	72	14	28	11	18	6	5	4
7	.77-.43	46	28	21	14	5	3	--	--	1	--
Filter	.43	--	139	--	12	--	--	--	--	5	--
Total		1543	549	352	144	114	51	42	25	24	20

(a) $\mu g/Nm^3$ for the ten most abundant elements detected
(b) Time run was initiated
(c) Based on total Pilat catch

TABLE 20. RESULTS[a] OF XRF ANALYSIS OF PILAT SAMPLE NO. 7

Date: 5/7/81 Time[b]: 1531 hrs. Volume: .2097 DNCM Mass Emission Rate[c]: 3.590 Kg/Hr

Stage	Size (μm)	Ca	Fe	Si	S	Al	Cl	K	Zn	Mg	Sn
1	50-32	78	111	25	41	9	--	4	8	1	--
2	32-15	59	59	15	25	3	--	2	7	--	--
3	15-5.4	438	46	45	35	15	--	9	12	5	7
4	5.4-2.7	654	48	78	35	33	--	18	--	8	9
5	2.7-1.5	785	65	124	45	56	--	29	7	12	12
6	1.5-.78	281	48	57	22	29	--	14	9	5	3
7	.78-.43	78	18	42	16	8	--	3	8	2	--
Filter	<.43	--	145	--	14	--	105	--	--	--	--
Total		2373	540	386	233	153	105	79	51	33	31

(a) $\mu g/Nm^3$ for the ten most abundant elements detected
(b) Time run was initiated
(c) Based on total Pilat catch

TABLE 21. RESULTS[a] OF XRF ANALYSIS OF SOURCE PARTICULATE CHARACTERIZATION SAMPLE NO. 1

Date: 5/4/81 Time[b]: 1532 hrs.

Element	Filter type					
	GF[c]	AA[d]	N[d]	FS[d]	TE[d]	GHIA[d]
Ca	3097±155	5239±573	4655±163	14383±9966	8205±676	5285±1818
Si	--	673±69	671±18	1614±1062	1014±76	574±334
Fe	380±26	377±20	325±19	1011±666	567±39	443±31
Al	--	342±33	351±8	737±461	514±52	269±165
S	152±27	188±26	167±12	478±361	280±3	161±89
K	11±1	155±19	132±5	404±276	240±2	149±57
Sn	49±1	76±7	64±3	206±141	118±7	65±22
Mg	--	75±12	65±0	158±99	106±12	60±35
Cl	113±26	92±37	34±0	156±115	86±7	48±28
Ti	31±7	55±4	48±3	126±78	75±2	56±20

(a) $\mu g/Nm^3$
(b) Time sampling initiated
(c) Average from a 5 and a 15 minute sample
(d) Average of a 1 and a 3 minute sample

TABLE 22. RESULTS[a] OF XRF ANALYSIS OF SOURCE PARTICULATE CHARACTERIZATION SAMPLE NO. 2

Date: 5/5/81 Time[b]: 1023 hrs.

Element	Filter type					
	GF[c]	AA[d]	N[d]	FS[d]	TE[d]	GHIA[d]
Ca	997±52	1435±309	1995±30	2184±306	2265+17	1779±813
Si	--	156±132	370±10	367±47	375±7	245±174
Cl	758±176	618±152	90±14	165±61	126±22	40±28
Fe	296±51	140±7	160±6	165±23	179±7	175±24
Al	--	--	207±7	197±29	209±7	138±102
K	--	79±14	102±10	104±12	109±10	92±44
Br	29±8	103±33	--	63±29	--	--
S	50±3	55±4	61±7	--	--	45±33
Mg	--	19±13	36±0	37±5	37±0	25±19
Sn	16±0	--	29±3	23±7	26±4	--

(a) $\mu g/Nm^3$
(b) Time sampling initiated
(c) Average from a 5 and a 15 minute sample
(d) Average of a 1 and a 3 minute sample

TABLE 23. RESULTS[a] OF XRF ANALYSIS OF SOURCE PARTICULATE CHARACTERIZATION SAMPLE NO. 3

Date: 5/7/81 Time[b]: 0937 hrs.

Element	Filter type					
	GF[c]	AA[d]	N[d]	FS[d]	TE[d]	GHIA[d]
Ca	1441±10	2744±263	2991±33	2747±48	2695±295	1158±90
Al	--	335±21	410±7	340±3	346±39	36±4
Cl	612±145	627±176	28±4	59±14	45±17	--
Fe	346±32	211±8	268±42	242±56	221±34	193±4
Al	--	171±21	218±4	164±2	170±22	36±4
S	67±15	110±8	128±7	103(e)	87±11	23±1
K	--	81±4	85±0	73±0	75±10	30±3
Sn	20±0	39±5	40±0	40±1	42±7	10±2
Mg	--	35±3	39±0	35±1	36±5	10±2
Ti	26±3	25±2	28±0	27±1	22±2	11±1

(a) $\mu g/Nm^3$
(b) Time sampling initiated
(c) Average from a 5 and a 15 minute sample
(d) Average of a 1 and a 3 minute sample
(e) Result of one measurement only

TABLE 24. RESULTS[a] OF XRF ANALYSIS OF SOURCE PARTICULATE CHARACTERIZATION SAMPLE NO. 4

Date: 5/7/81	Time[b]: 1119 hrs.					
	Filter type					
Element	GF[c]	AA[d]	N[d]	FS[d]	TE[d]	GHIA[d]
Ca	1403±15	1403±15	2803±436	2888±550	2311±253	1172±12
Si	--	318±17	359±46	355±59	298±24	78±3
Fe	271±40	218±25	195±32	214±31	189±24	211±31
Al	--	156±5	187±24	170±29	149±15	35±1
Cl	370±103	--	19±5	36±11	20±4	--
S	73±1	120±1	117±29	--	113±17	21±1
K	--	84±4	76±13	79±16	75±11	29±1
Mg	--	38±0	39±6	35±5	30±3	8±1
Ti	22±2	23±2	25±3	33±12	19±1	11±1
Sn	21±2	37±3	40±4	41±9	37±8	10±4

(a) $\mu g/Nm^3$
(b) Time sampling initiated
(c) Average from a 5 and a 15 minute sample
(d) Average of a 1 and a 3 minute sample

TABLE 25. RESULTS[a] OF XRF ANALYSIS OF SOURCE PARTICULATE CHARACTERIZATION SAMPLE NO. 5

Date: 5/7/81 Time[b]: 1433 hrs.

Element	Filter type					
	GF[c]	AA[d]	N[d]	FS[d]	TE[d]	GHIA[d]
Ca	1762±300	2834±493	2453(e)	2711±67	4456±3356	2631±1148
Si	--	294±163	368(e)	368±6	637±474	323±212
Fe	219±24	237±30	191(e)	245±17	422±319	344±101
Al	--	191±26	191(e)	179±5	306±23	146±97
S	115±10	134±28	105(e)	85(e)	219±176	108±77
K	--	101±20	75(e)	81±2	145±111	79±40
Cl	292±90	--	12(e)	34±10	62(e)	10±6
Mg	--	44±6	35(e)	38±3	61±46	32±21
Sn	28±4	40±6	35(e)	42±6	63±48	40±17
Ti	28±4	26±3	25(e)	29±2	41±33	26±11

(a) $\mu g/Nm^3$
(b) Time sampling initiated
(c) Average from a 5 and a 15 minute sample
(d) Average of a 1 and a 3 minute sample
(e) Result of one measurement only

This is consistent with gaseous source samples and Pilat analyses for the bypass mode. Further indication that the amount of Cl collected is highly dependent on the filter media is evident from the characterization results for both modes where a minimum of Cl was collected in all filter catches except the glass filter and the AA. For the characterization sample collected on Tuesday, the average Cl catch from the remaining four types of filters is only 105 $\mu g/Nm^3$. At this concentration, particle-related Cl^- would then be the sixth most abundant element, which is reasonable when compared to the results of the Pilat 2 sample disregarding the filter Cl catch. The association of higher amounts of Cl with the glass fiber filters, as with the Pilat filter, indicates the collection of gaseous HCl on particles.

Process Sampling

A record of some critical process parameters was maintained during the study. Table 26 shows the fuel and raw product feed rates for the sampling times. With the exception of a short period of time on the bypass mode day when gas was fired instead of coal, smooth flow process conditions prevailed. The results of additional sample acquisition and analyses of process reagents and products are shown in Table 27. Based on the four values determined from representative sampling of the conditioning tower inlet, the average Cl^- and $SO_4^=$ concentrations of the water were 11.97 and 71.15 µg/ml, respectively. From the conditioning tower input rate of 85 gal/min, and a density of 8.3 lb/gal, the tower used 42,330 lb/hr. In terms of Cl^- and $SO_4^=$, the inputs to the tower were 0.54 and 3.24 lb/hr, respectively. Table 27 also includes Cl^- and $SO_4^=$ analysis of the milled raw product which is fed to the kiln. There appears to be little difference in Cl^- and $SO_4^=$ in the feed powder, with an average 0.31 and 0.65 mg/g of Cl^- and $SO_4^=$ for the raw product, respectively.

Several sludge samples were acquired during the bypass mode operation of the conditioning tower. Four samples, acquired after equilibrium of the mode

TABLE 26. PROCESS DATA

Date	Time	Coal usage (tons/hr)	Feedstock (tons/hr)	Opacity[a]
5/4	--	9.6	130	
5/4	--	9.3	129	
5/5	0902	9.7[b]	120	10-15
5/5	1035	9.9	121	4
5/5	1238	9.9	128	3
5/5	1357	9.9	127	4
5/5	1454	9.9	127	4
5/7	0949	9.8	121	2.0
5/7	1048	9.8	121	1.5
5/7	1149	10.0	127 (c)	1.5
5/7	1247	10.0	120	1.5
5/7	1345	10.0	121	2.3
5/7	1447	10.0	122	2.0
5/7	1547	10.0	127	3.0

(a) Average transmissometer reading
(b) Gas used for firing for approximately 15 min
(c) Usage was fluctuating

TABLE 27. RESULTS OF CHEMICAL ANALYSES OF PROCESS SAMPLES

Sample No.	Date	Description	Concentrations (µg/ml) Cl^-	NH_3	$SO_4^=$
CA	5/5	Conditioning tower inlet H_2O[a]	11.97	N.D.	70.51
CC	5/5	Conditioning tower inlet H_2O	11.83	N.D.	71.01
CD	5/5	Conditioning tower inlet H_2O	12.05	N.D.	71.58
CE	5/5	Conditioning tower inlet H_2O	12.01	N.D.	71.52
CF	5/5	Quarry H_2O	12.73	N.D.	73.10
CG	5/7	Quarry H_2O	13.50	N.D.	73.35

Sample No.	Date	Time	Description	Concentrations (mg/g) Cl^-	NH_3	$SO_4^=$
CH	5/5	0945	Conditioning tower sludge[b] (129 g)	1.42	.02	.92
CI	5/5	1056	Conditioning tower sludge (102 g)	2.06	.08	1.17
CJ	5/5	1245	Conditioning tower sludge (102 g)	2.60	.04	1.42
CK	5/5	1406	Conditioning tower sludge (104 g)	2.33	.03	1.11
CL	5/5	1457	Conditioning tower sludge (108 g)	2.15	.03	1.79
CM	5/5		Mill mode product[c] (95 g)	.29	.01	.68
CN	5/7		Bypass mode product (84 g)	.31	.01	.63

(a) Clarified water used in temperature conditioning tower.
(b) Waste product consisting of cooling water and kiln feed powder.
(c) Powder fed to riser system and kiln.

TABLE 28. AMMONIA CONTENTS OF RAW PRODUCTS

Run No.	Description	Gas volume (SCF)	Solid weight (g)	Temperature (°F/°C)	NH_3 Gas (µg)	NH_3 Solid (µg)	% Evolution
1	Air blank	1.924	--	148/64	30.43	--	--
2	ESP-Solid	--	202.0	--	--	4245.8	--
3	ESP-Solid	4.908	204.0	150/65.5	12.17	3865.8	.31
4	ESP-Solid	4.113	205.3	200/93.3	204.3	3898.9	5.0
5	ESP-Solid	4.074	201.2	250/121	147.7	2528.7	5.5
6	ESP-Solid	1.196	98.2	292/144	178.5	1476.9	10.8

had been achieved, showed an average of 2.28 and 1.37 mg/g of Cl^- and $SO_4^=$, respectively, and a 35.9% moisture average. Based solely on the input of conditioning water and the raw feed rate, the levels of Cl^- and $SO_4^=$ in the sludge can be predicted to be 0.20 mg/g and 2.68 mg/g, respectively. The average of four samples from Table 27 shows that 2.28 mg/g and 1.37 mg/g were present in the sludge. The contribution of Cl or S from the cooling water can, therefore, be taken as negligible.

As determined by XRF analysis of several respresentative coal samples, the Cl and S content of the coal utilized in the kiln were found to be 0.118 and 0.619% by weight, respectively. Based on the average coal usage rate of 9.9 tons/hr during the bypass mode, this results in a production of 24.06 lb/hr of HCl, assuming all Cl in the coal is converted to HCl. The mass emission rate for S is 122.54 lb/hr, equivalent to 245.08 lb/hr of SO_2.

As indicated in Table 13, the measured average mass emission rates of total HCl and SO_2 by conventional measurements were 16.9 and 66.9 lb/hr, respectively, for Tuesday. This corresponds to 70.2% of the coal Cl and 27.3% of the coal S being emitted from the source, assuming all of those emissions were from the coal.

For the mill mode, the projected mass emission rate of HCl and SO_2 based on the coal analysis, were 24.3 and 247.6 lb/hr, respectively. Based on the measured emission rates as presented in Table 13, only 51.9 and 5.4% of the HCl and SO_2 projected from the coal analyses were emitted on Thursday. Absorption of the SO_2 during the mill mode operation appears to exceed 90% while nearly 48% of the HCl appears to pass through the mill.

Analyses of the raw product being fed to the riser system were conducted on several aliquots of the material. Purified laboratory air was pulled over the powder at various temperatures and this purge air was pulled through a 0.1 N H_2SO_4 solution to retain any liberated NH_3. Temperatures ranging from

ambient (25°C) to 146°C (the ESP temperature during the bypass mode) were used. The results of these measurements are shown in Table 28. The data reflect the dependence of the NH_3 absorption and/or desorption on temperature. Only 0.3% of the NH_3 would evolve at 66°C (150°F), below the ESP temperature during the mill mode. However, 5% of the NH_3 evolves at 93°C (200°F), which is slightly above the 82 to 88°C (180 to 190°F) temperature measured at the stack during the mill operation sampling. At 96°C (205°F), the temperature of the stack gas measured during the bypass mode, over 10% of the NH_3 would evolve.

SECTION 5

DISCUSSION

The gas and particle measurements and characterizations performed indicate that an opaque plume results from the reaction of HCl gas and NH_3 gas, or the condensation and particle growth of NH_4Cl gas exiting from the source. The following facts lend support to this conclusion:

1) During the bypass mode gaseous NH_3, HCl, and S were emitted at average rates of 4.23, 6.92, and 33.4 lb/hr, respectively, as measured by conventional measurement methods. The rates of total NH_3 and HCl (gas and particles) were 4.91 and 14.13 lb/hr, respectively, measured by the same method.

2) During the same sampling period, the modified method of sampling showed gaseous NH_3 and HCl emission rates of 4.66 and 10.17 lb/hr, respectively. By the same methods, the total NH_3 and HCl emissions (gas and particles) were 6.55 and 13.38 lb/hr, respectively.

3) According to conventional measurements, 86.1 and 49.0% of the NH_3 and HCl, respectively, were emitted as gas-phase components during the bypass mode. As measured by the modified methods, 71.1 and 76.0% of the total NH_3 and HCl, respectively, were emitted as gas-phase components.

4) Analysis of a triple filter sample (TFT-11) acquired in the plume on the bypass mode day indicated retention of 1.86, 1.13, and 12.5 moles of HCl, NH_3 and S, respectively. The first filter, assumed to collect particles only, contained 1.25 moles of HCl, .75 moles NH_3, and

.08 moles S. The second filter retained 12.4 moles of S, .61 moles of HCl and no NH_3, while the third filter retained .39 moles of NH_3 and no HCl or S. Thus 67.2% of the total collected HCl, 66.4% of the total NH_3 and only 0.6% of the total sulfur were collected as particulate components.

5) A second triple filter train (TFT-12) yielded in similar results: 56.7 and 25.3% of the total HCl and NH_3 collected, respectively, were retained on the first (particle) filter. For this second filter train only .06 moles of S were collected on the first filter. The molar ratios of HCl to NH_3 for the first filters of these two samples were 1.67 and 1.35. There appeared to be little association of NH_3 with S as evidenced by the negligible amount of S on the first filter and the absence of NH_3 on the second filter where the SO_2 was collected.

6) Analysis of the SEM sample depicted in Figure 9 indicated a predominance of 0.2 to 0.6 μm particles during this bypass sampling time period. Analysis of these particles and their behavior to the electron beam gave strong indication that they were NH_4Cl crystals.

7) Examination of the particle characterization samples indicate that, except where gaseous HCl absorption may have occurred, little particulate Cl^- is present in the bypass emissions. Such HCl absorption appears to have occurred on the filter of the Pilat sample acquired during the bypass mode and by the glass filter and cellulose filter of the particle characterization samples for the bypass mode as well.

8) The results of the LIDAR measurements conducted during the bypass mode support the evidence of a reactive plume inasmuch as the opacity increased with distance from the stack, while dilution of the plume should result in a decreasing opacity if no ongoing reactions occur.

While HCl gas was emitted in both the mill and bypass modes, little gaseous NH_3 was emitted during the mill mode. Temperature-dependence studies of NH_3-particle absorption suggest that emission of NH_3 during the bypass mode may be due mainly to the higher temperature of the precipitator than in the mill mode.

While the preponderance of the plume data indicate NH_4Cl formation, some discussion of the SEM filter analyses which showed the presence of sulfite ion in the plume must be presented. The SEM filter pulled at 3:06 p.m. on the bypass mode day indicated the presence of sulfur-containing particles within the 0.2 to 0.8 μm particle size range. The SEM sample that showed the presence of the NH_4Cl particles was acquired at 3:28 p.m. on the same day. As this particle variation occurred within half an hour, a highly reactive and possibly variable plume is present. The presence of NH_3 and SO_2 in a plume can result in the formation of visible particles as shown in the cement plant study at Glens Falls (5). This reaction can occur readily when water droplets are formed by condensation in a plume. Such a reaction could have taken place at this plant if, for example, a sudden introduction of moisture into the plume occurred due to an upset in the conditioning tower operation. From the analysis of the TFT filters, no other samples detected $S^{=}$, which leads to the conclusion that, while possible, the reaction of NH_3 with SO_2 in this plume occurred infrequently.

For this source, the general lack of association of NH_3 with SO_2 in the plume samples seems to eliminate the type of plume reaction such as discussed by Chadbourne (20). At the same time, these data support the formation of NH_4Cl particles in the plume as a result of a reaction between gaseous HCl and NH_3. That such a reaction is known to occur has been well documented. Recent studies (21) show that reaction of NH_3 with SO_2 is minimal in the absence of

water droplets. The same is not true of HCl and NH_3, which react readily in the gas phase. The source emissions and reactive plume depicted by this study coincide well with the work of Su with respect to several details, namely:

1) There is an induction time involved in the laboratory reaction of NH_3 and HCl which can be related to the detached nature of the plume.
2) Strong evidence was found that a narrow size range of NH_4Cl particles is formed due to a nucleation burst; this was evidenced by the NH_4Cl particles (0.4 μm and smaller) detected by SEM.
3) There is also a great similarity in the NH_4Cl particle size, as the quoted work involves particles predominantly in the range from 0.1 to 1 μm.
4) Under hydrous conditions particles of NH_4Cl were detected only when the product of the NH_3 and HCl concentrations was 10 ppm^2 or greater. For the bypass mode this average product was 201 ppm^2, while the same product for the mill mode was 31 ppm^2. Considering the dilution which can occur as the plume disperses, the 201 ppm^2 product would likely result in particle formation while the 31 ppm^2 product likely would not.

While the operation schelule limited the number of samples acquired during the bypass mode, the detached opaque plume present during this mode can be taken to be NH_4Cl. From the extensive gas-particle measurement and characterization data acquired during the sampling period, the emission of gaseous HCl and NH_3 and their subsequent gas-phase reaction to form NH_4Cl particles can be shown to be the cause of the opaque plume. The numerous physical and chemical similarities of an indepedent laboratory study of NH_3 reactions with SO_2 and HCl to this source-ambient air system also supports this conclusion.

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